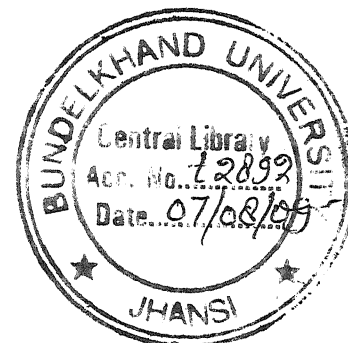


SYNTHESIS OF ORGANOMETALLIC COMPOUND OF CHALOGEN



**A THESIS
SUBMITTED TO
BUNDELKHAND UNIVERSITY
FOR THE
AWARD OF DEGREE OF
DOCTOR OF PHILOSOPHY
IN
CHEMISTRY**



**BY
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INDIA
JUNE 2005**

Dedicated
To My
Parents, Wife,
Brother
&
Sister

Dr. Yogesh Pandey
Reader in Chemistry Bipin Bihari
(P.G.) Science College, Jhansi.

Date : 10/06/05

CERTIFICATE

Certified that the work embodied in this thesis entitled **Synthesis of Organometallic Compounds of Chalogen** is the result of original researches carried out by **Mr. Anil Kumar**, Lecturer in Chemistry B.B.C. (P.G.) College, Jhansi under my supervision and is suitable for submission for the award of Ph.D. Degree of University of Bundelkhand, Jhansi.



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S. Srivastava


Prof. Shekhar Srivastava

DECLARATION

I here by declare that the thesis intitlled **Synthesis of Organometallic Compounds of Chalogen** being submitted for the degree of **Doctor of Philosophy** to the Bundelkhand University, Jhansi (U.P.), is an innovative piece of work carried out with utmost dedication by me, and to the best of my knowledge and belief it has not been submitted elsewhere.

Place :- Jhansi

Date : ...10/06/05...


Anil Kumar
(Lect. in Chemistry,
B.B.C. Jhansi)

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CHAPTER - I

INTRODUCTION

Organometallic chemistry is a study of the compounds containing at least one direct metal-carbon bond. The term 'metal' is, however, difficult to define with precision. Elements having electronegativity less than that of carbon can be considered as metals, giving rise to a carbon metal bond with a differential higher electron density around the carbon atom. Thus, the organometallic compounds contain an anionic carbon.

The importance of organometallic compounds is manifold. The field of synthetic organic chemistry is well established. Further, the electron deficient bridging structure of metal alkyls, the sandwich configuration of ferrocene type compounds¹ and the unusual metal valence state of certain organometallic compounds² have necessitated a drastic revision in the old concepts of structure and bonding and have played a prominent role in advancing new theories of valency. The biological activity of many organometallic compounds have been a new asset to the mankind.

The organometallic chemistry of many main group elements are well known and exhaustively covered in several reviews and books³⁻¹⁴. In contrast to this, the organometallic chemistry of group VI A elements, in general, and tellurium in particular, has been little studied.

The first organic derivative of tellurium, dialkyltelluride, was prepared by Wohler in 1840¹⁵. At first, the organotellurium chemistry remained unexplored but later on, it was pursued mostly as an extension to corresponding selenium

chemistry. But now it is quite clear that there are at least as many dissimilarities as there are similarities in the chemical behaviour of selenium and tellurium. Some of the workers who greatly enriched the knowledge of organotellurium chemistry include Lederer (1910-1920); Morgan, Drew and co-workers (1920-1935); Petraghani demoura campos and co-workers (1960-70) and Schumann and co-workers (since 1963). Some recent creditable work by Irgolic have appeared in the form of several reviews and books¹⁶⁻¹⁸.

Organotellurium compounds are highly toxic and the effect is often cumulative¹⁹⁻²². Large doses paralyses nerve structure and cause headache, nausea and eczema²³⁻²⁴. Continued inhalation of dimethyl telluride and other volatile tellurium compounds induces and unpleasant halitosis and debility and causes headache²⁵.

A paper describing the inhibitory action of cyclic tellurium compounds on the growth of bacteria appeared in 1922²⁶. Taniyama and co-workers found that diaryltellurium dihalides possess a strong antibacterial action²⁷. Oefele published a review on therapeutic agents containing tellurium²⁰. Patents covering organic tellurium compounds have also been reported²⁸.

Tellurium is present in the earth's crust to the extent of 2×10^{-7} Percent by weight. However, it is generally obtained as a by-product of mining and processing operations of other ores. Today tellurium accumulates as a by-product of the electrolytic copper refining process. The anode sludge can contain

up to 8% tellurium in addition to Se, Cu, Ag, Au, and Platinum group metals. Density of crystalline metals at 449.8°C to a dark liquid and boils at 1390°C²⁹. A detailed discussion of the physical properties of tellurium is available in the literature²⁸.

The properties of the elements in subgroup VIA of the periodic table O, S, Se, Te, and Po undergo striking transition as the group is descended. The chemical behaviour of the group passes from that of the typical non metals O and S to the typical metal Po. A systematic change is also observed in the structure of the elements from diatomic molecules, through ring and chain molecules to a simple lattice compound of polonium atom. A corresponding transition in electrical properties accompanied the structure evolution. Thus, oxygen and sulphur are insulators, Se and Te are semiconductors and Po show metallic conduction.

The industrial applications of tellurium and its compounds have been described by Champness²⁹, Nachtman³¹, Aborn³¹ and Cooper³². Their applications as rubber vulcanization, accelerators, antiknock agents, antioxidants, insecticides, lubricating oil additives, gel forming clays, curing agents for ethylene propylene terpolymers, Photoconductors, therapeutic agents, dye intermediates and wetting agents are well known¹⁶.

The ecological aspects of tellurium in human and animals health, the toxicity and metabolism of tellurium compounds and the interaction of sodium tellurate with Hg, Cd, Se, Be and As have been reviewed¹⁷.

Electronic Configuration and Stereochemistry

The elements of group VIA have a general electronic configuration $[X] ns^2 np_x^2 np_y^1 np_z^1$ (where x = inert gas core and 'n' = 2 to 6 from oxygen to polonium) and tend to attain an inert gas configuration by gaining or sharing two electrons. E^{2-} Ion, however, exists in case of oxygen only. The More electropositive elements S, Se and Te form only a few compounds which are more than 50% ionic. The formal oxidation states of II, IV are known for tellurium and are summarized in table I along with the possible stereochemistry.

Table : 1

Valency	CO. NO.	No. of bonds	No. of lone pairs	Geometry	Hybridisation	Examples
II	2	2	2	Angular	sp^3	R_2Te , $RTeX$
	3	3	2	Pyramidal	sp^2d	$[RTeX_3]$
	4	4	2	Square- Planner	sp^3d^2	$Te[SC(NH_2)_2]Cl_2$, $PhTeX_2[SC(NH_2)_2]$
IV	4	4	1	Trigonal	sp^3d	R_2TeX_2 , $RTeX_3$
				Bipyramidal		R_4Te
				Tetrahedral		$R_3Te^+X^-$
	5	5	1	Square- pyramidal (4)	sp^3d^2	$[RTeX_4]^-$, $RTeX_3.L$ (L=Monodentate)

	6	6	1	Octahedral	sp^3d^3	$[R_2TeX_4]^{2-}, RTeX_3 \cdot L$ (L=Bidentate)
	7	7	1	Distorted pentagonal bipyramidal	sp^3d^4	$RTe, [Et_2NCS_2]_3$
	8	8	1	Distorted dodecahedral	sp^3d^5	$Te(Et_2NCS_2)_4$
VI	6	6	no	Octahedral	sp^3d^2	$C_2F_5TeF_4Cl,$ $(C_2F_5)_2TeF_4$
	8	8	no	-	sp^3d^4	TeF_8^{2-} $TeF_6 \cdot 2R_3N$

Te Ground State	
Te (II)	
Te (IV) 1 st Excited State	
Te (VI) 2 nd Excited State	

Fig. 1 : Possible oxidation states in tellurium

Te has in the ground state, two unpaired electrons and hence oxidation state(II) is well known. In such compounds one 's' and three 'p' orbitals hybridise, giving four sp^3 hybrid orbitals, of which, two are occupied by lone

pairs and the remaining two have bonding electron pairs. The geometry is thus 'V' shaped(Fig.2).

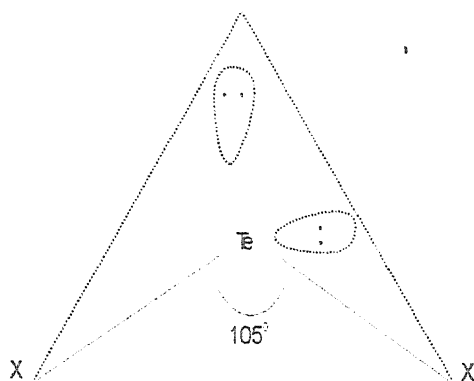


Fig. 2: V-shaped structure for Te(II) compounds

In the first excited state, compounds with tellurium in oxidation state (IV) are obtained by uncoupling the p_x^2 electrons: one of them being promoted to the empty d orbitals, resulting in the formation of five of sp^3d hybrid orbitals of equivalent energy, directed trigonal bipyramidally in spaces about the metal atom (Fig.3).

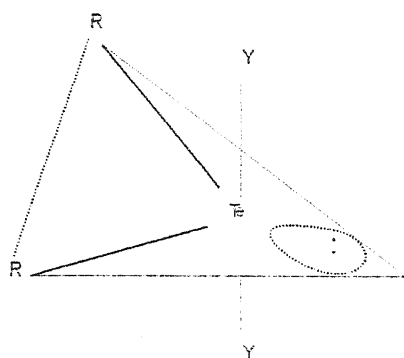


Fig.3: Trigonal bipyramidal structure for Te(IV) compounds

In the first excited state, coordination number greater than four is achieved by accepting electrons with suitable donors in the empty d-orbitals. The for-

mation of penta-and hexa-coordinated molecules is visualises on the basis of sp^3d^3 and sp^3d^2 hybridisation with one lone pair of electrons resulting in pseudooctahedral and octahedral structures respectively³³⁻³⁵. (Fig.4 and 5).

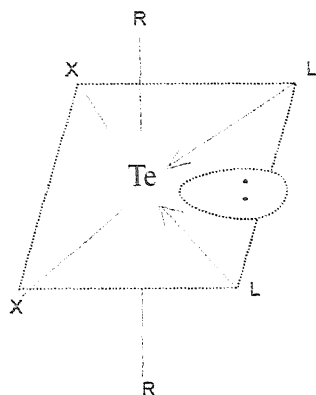


Fig.4: sp^3d^3 pseudooctahedral

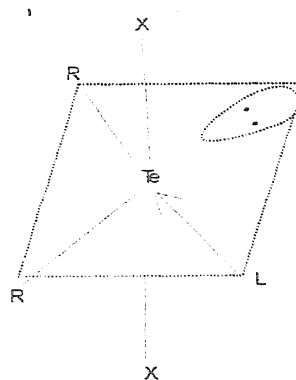
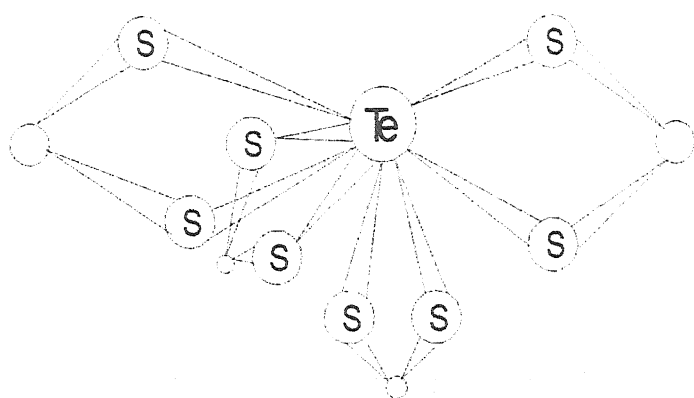


Fig.5: sp^3d^2 Octahedral

Coordination number greater than six are rare. A sp^3d^4 hybridised tellurium dithiocarbamate with stereochemically inert lone pair of electrons has been reported³⁶. Hepta and octacoordinated tellurium atom having sp^3d^4 and sp^3d^5 hybridisation have also been reported by steinar et al³⁷⁻³⁸. (Fig.6).



(All Et_2 N-groups are omitted and the smallest spheres represent carbon atom)

Fig.6: $Te(Et_2NCS_2)_4$

In the second excited state, all the six electrons of outer most orbit of tellurium get uncoupled resulting in sp^3d^2 orbital formation, which are directed

octahedrally about the metal atom³⁹⁻⁴⁰.

TeF_6 , $\text{C}_2\text{F}_5\text{TeF}_4\text{Cl}$ and $(\text{C}_2\text{F}_5)_2\text{TeF}_4$ having regular octahedral structure have been confirmed by IR (Fig.7)

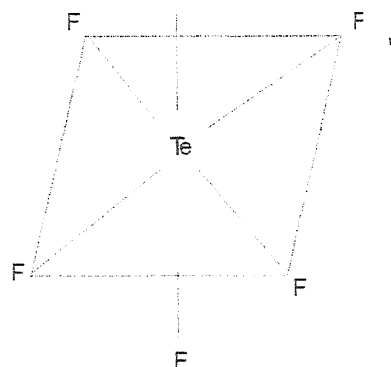


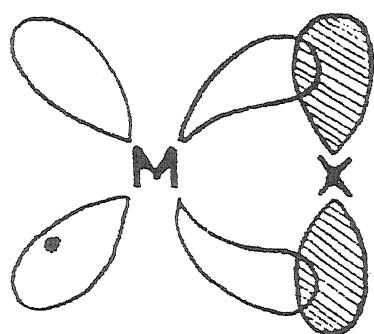
Fig.7: Regular octahedral structure of TeF_6

Low lying d-orbitals in the outermost valency shell of tellurium are thus involved in the expansion of covalency. The stable coordination compounds with electron donors may be formed when a pronounced stabilisation occurs through the participation of vacant d-orbital. The additional bonds in expansion of bi-and tetra covalency of tellurium may be of the following types:

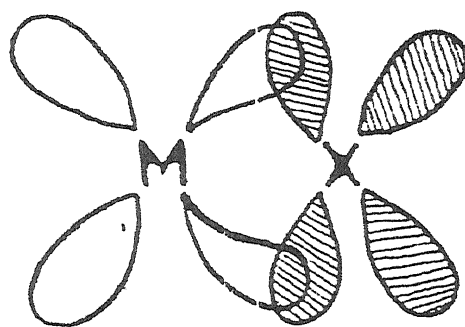
$\text{D}\sigma$ – bonding : In which there is an overlap of s-orbital of the donor atom with d-orbital of the metal atom e.g., in $\text{R}_2\text{TeX}_2 \cdot n\text{NH}_3$.

$\text{d}\pi$ – bonding: Here the empty d-orbital of the metal overlap with the filled p or d orbitals of adjacent donor atom having available lone pair of electrons, which gives a partial double bond character to the donor metal sigma bond.

This could be schematically represented as in Fig. 8.



$d\pi - p\pi$ interaction



$d\pi - d\pi$ interaction

Fig. 8

Organotellurium compounds

The first organotellurium compound, diethyl telluride, was synthesised by woehler in 1840. Since then many reports have appeared which deal with various aspects of organotellurium chemistry. The organic chemistry of tellurium up to 1974 has been exhaustively reviewed by Irgolic¹⁶.

Methods of preparation of Te-C bonded molecules :

In most of the reactions tellurium metal, tellurium hydride, sodium-and other metal tellurides, tellurium tetrachloride and organic tellurium compounds have been used to synthesise Te-C bonded molecules. A short account of these methods is given below:

A. Elemental tellurium :

A number of organotellurium compounds are synthesised directly from elemental tellurium. The reactions resulting in the formation of the least one C-Te bond are summarized in (Fig.9).

B. Tellurium hydride :

There are a few recent reports of the use of tellurium hydride as a reagent to introduce tellurium in organic molecules^{17,41}.

C. Sodium and other alkali metal tellurides :

Alkali metal tellurides are easily alkylated by organic halides. Upon mixing stoichiometric amounts of diacetylenes with sodium telluride and hydrolysing the product, 2,5-disubstituted tellurowhenes are isolated. With aliphatic alcohols at 300-150°, alkali metal tellurides give tellurols and tellurides (Fig.10).

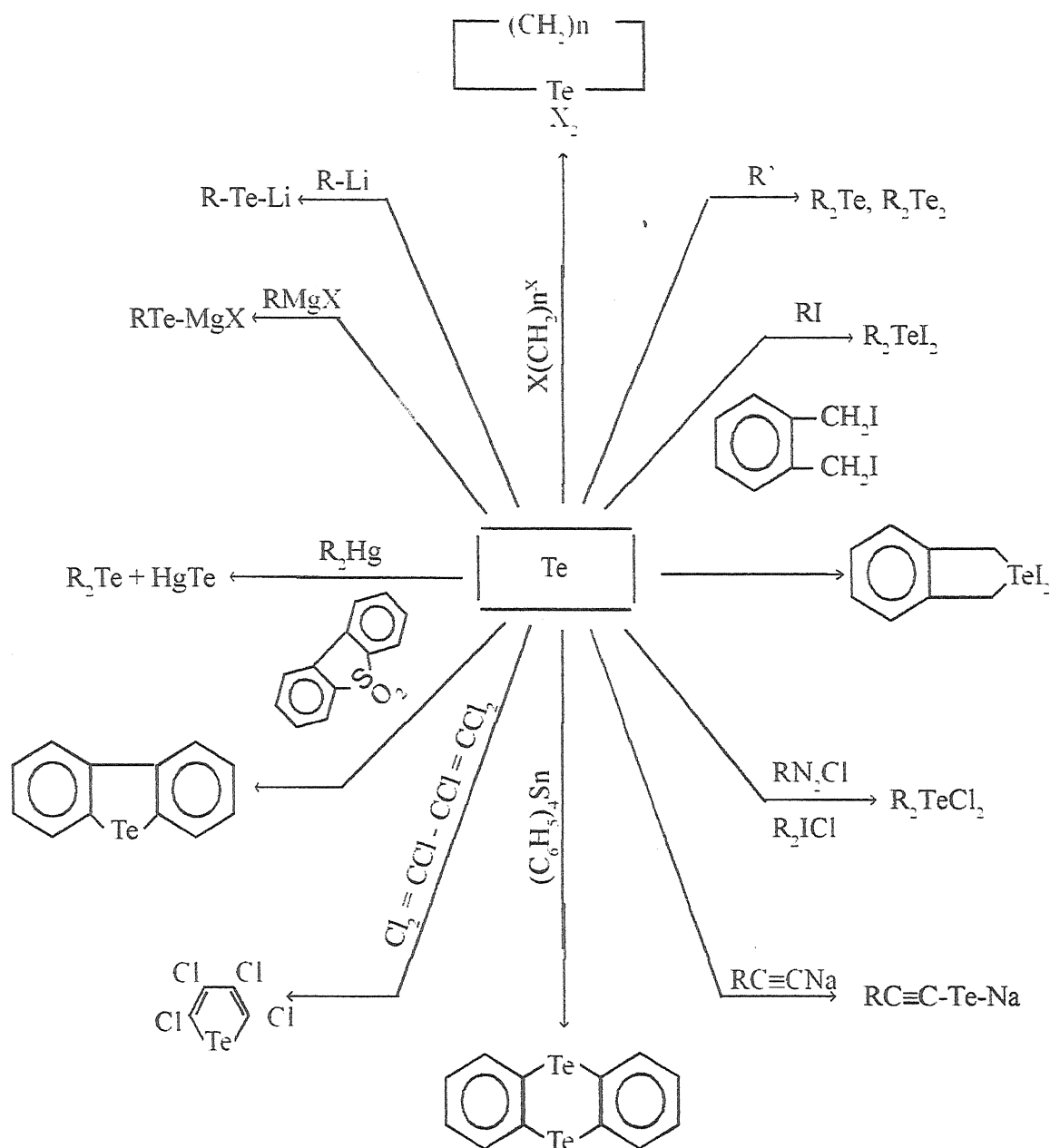


Fig.9

D. Tellurium tetrachloride :

There are a large number of reactions taking place between anhydrous tellurium tetrachloride and organic reagents which proceed with formation of molecules containing at least one carbon-tellurium bond (Fig.11).

E. Organic tellurium compounds :

A general outline of the reactions of organotellurium compounds leading to the formation of additional carbon - tellurium bonds is given in Fig. 12.

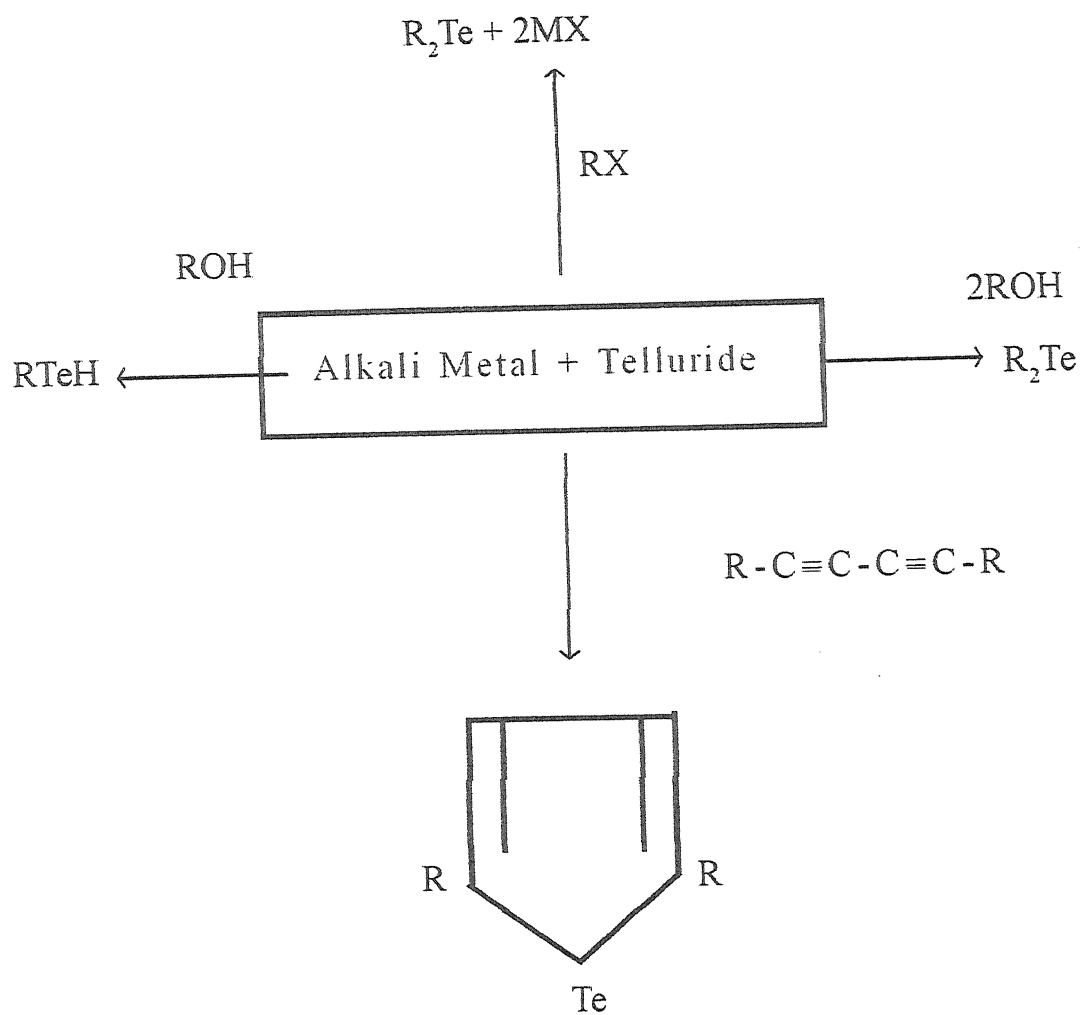


Fig.10

The book "the Organic Chemistry of Tellurium" by Irgolic covers the organotellurium literature during the time span from 1840, When Wohler reported the first organotellurium compounds, through 1971. The organotellurium chemistry after 1971 has progressed unexpectedly. In the present investigation, a number of organotellurium compounds, have been prepared and characterise. It would, therefore, be appropriate to give a short account of the chemistry of organotellurium compounds before describing the details of the present investigation.

On the basis of oxidation states, the organotellurium compounds may be classified into four main headings :

- (i) Oxidation state zero,
- (ii) Oxidation state two,
- (iii) Oxidation state four and
- (iv) Oxidation state six

(i) Compounds in oxidation state (0)

In 1973, first such compounds $[(C_6H_5)_3P]_2Te$ was prepared in 30% yield, when tellurocyanates reacted with triphenylphosphine in acetonitrile solution on presence of lithium perchlorate. This zero valent compound decomposed at $83-85^\circ C^{42}$. The structures of $[(CH_3)_3P]_2Te$ and $[(CD_3)_3P]_2Te$ have also been suggested on the basis of IR and Raman spectra data⁴³.

(ii) Compounds in oxidation state(II)

These includes tellurols (RTeH), tellurenyl compounds (RTeX), tellurides (R_2Te) and ditellurides (R_2Te_2).

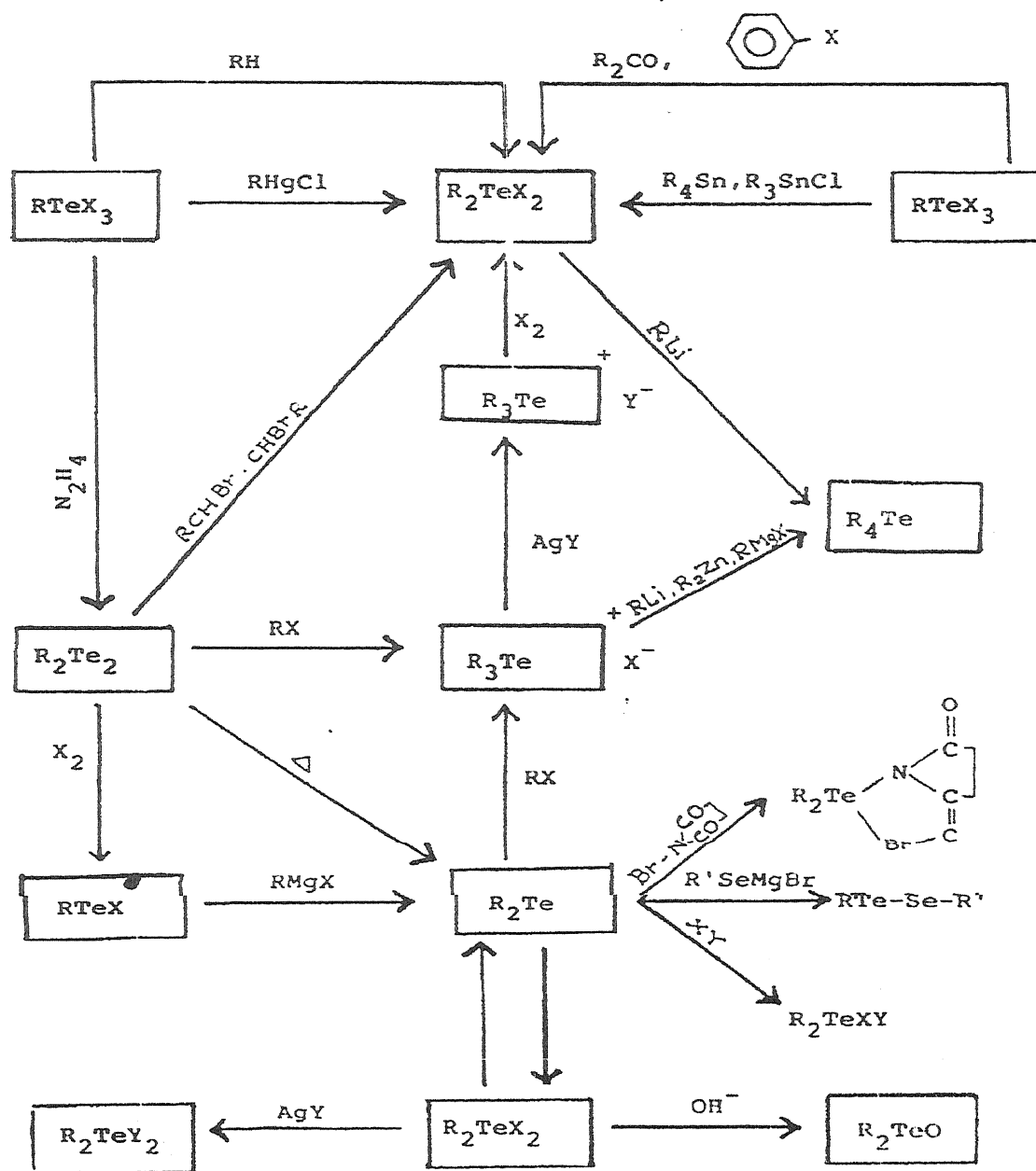


Fig. 12

Tellurols: Our knowledge about these compounds is limited owing to the exceedingly unpleasant odour, especially in case of the alkyl derivatives. How-

ever, methanetellurol and trideuteriomethanetellurol have been prepared by the hydrolysis of dimethyl detelluride⁴⁴. Lederer reported that benzene tellurol reacts with mercuric chloride to yield $C_6H_5\text{-Te-HgCl}$ ⁴⁵.

Tellureny Compounds: Aliphatic $R\text{TeX}$ are still unknown. With the exception of 2-naphthyltellurium iodide, it has not been possible to isolate other aryl tellurium halides. However, in solution, aromatic derivatives can be prepared⁴⁶. X-Ray structural analysis established the structure of 2-formylphenyl tellurium (II) derivatives as shown in Fig.13.

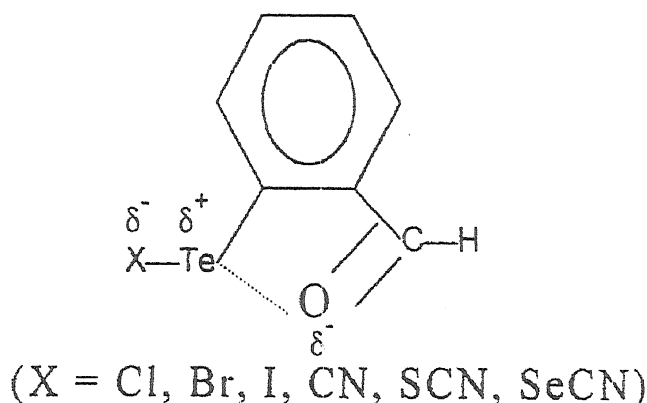


Fig. 13

$PhTeCN$ has been prepared through reductive cyanation of aryltelluriumtrichloride and from the reaction of aryltelluriumbromide with KCN ⁴⁷. The reactivity of 2-naphthyltellurium iodide has also been reported⁴⁸⁻⁴⁹.

Tellurides: Synthesis and reactivity of diorganyltellurides are shown schematically in (Fig.14), which also includes several new routes for preparation of symmetrical⁵⁰⁻⁵². and asymmetrical^{53, 17, 54-57} tellurides. Several tellurides, with two

schemed elow (Fig.15).

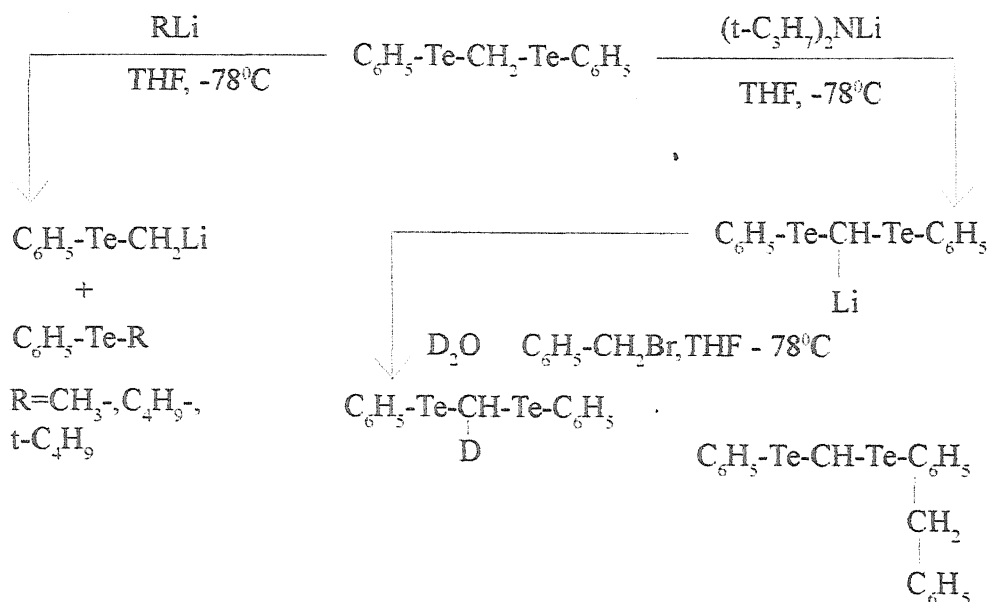


Fig. 15

The case with which bis (organo) telluriumdihalides are formed, lead to the investigation of the tellurides as dehalogenating agents⁵⁹. Lederer prepared a number of adducts of diphenyltellurides and dialkyltellurides⁶⁰⁻⁶¹. The structure of tellurides have been determined using UV, PMR and mass spectral data⁶²⁻⁶⁴.

Ditellurides: The first unsymmetrical diorganyl ditelluride, perfluorobutylpentafluoroethyl ditelluride, was formed in a reaction between tetrafluoro ethylene and $\text{Te}_4(\text{AsF}_6)_2$ or $\text{Te}_6(\text{AsF}_6)_2$ ⁶⁵. Recently, some new symmetrical diarylditellurides have been reported⁶⁶⁻⁷⁰. All the ditellurides are orange to red solids except methyl derivatives. Fission of Te-Te bond is brought about by halogenolysis with the formation of corresponding organotellurium (II) halides. Thermally, ditellurides decompose of R_2Te and Te ⁷¹⁻⁷². The struc-

ture of bis(4-chlorophenyl) ditelluride has been determined by single crystal X-ray analysis⁷³ (Fig. 16).

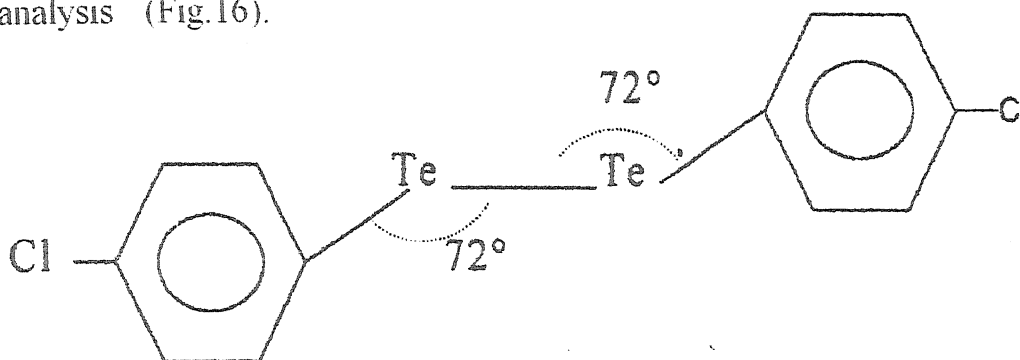


Fig. 16

2-alkoxy ethyl aryl tellurides $4\text{-R}^1\text{C}_6\text{H}_4\text{TeCH}_2\text{CH}_2\text{R}^2$ ($\text{R}^1 = \text{H, Me}$, $\text{R}^2 = \text{OMe, OEt}$) were obtained in 70-80% yield by the reaction of 1-bromo-2methoxy ethane or 1-bromo-2ethoxy ethane with arene telluralate anion. These telluride were converted to their corresponding TeCl_2 which on treatment with $\text{NaOCH}_2\text{CF}_3$ in $\text{CF}_3\text{CH}_2\text{OH}$ medium gave the corresponding bis (2,2,2-trifluoroethoxides) in 70-80% yields⁷⁴.

$(2\text{-RN:CHC}_6\text{H}_4)_2\text{Te}$ ($\text{R} = \text{alkyl, aryl}$) were prepared in $\geq 70\%$ yield by condensing $(2\text{-HCOC}_6\text{H}_4)_2\text{Te}$ with amines. X-ray analysis of $(2\text{-RN:CHC}_6\text{H}_4)_2\text{Te}$ ($\text{R} = o\text{-MeOC}_6\text{H}_4$) showed one intramolecular $\text{Te} \leftarrow \text{N}$ coordination (2.702 \AA) in crystal¹²⁵ Te NMR spectroscopy showed a trans coordination process occurring via rapid cleavage and formation of $\text{Te} \leftarrow \text{N}$ bonds⁷⁵.

The ditelluro ethers $o\text{-C}_6\text{H}_4(\text{TeMe})_2$ was prepared from $o\text{-C}_6\text{H}_4\text{Br}_2$ and LiTeMe in THF and $o\text{-C}_6\text{H}_4(\text{TePh})_2$ was obtained similarly from $o\text{-C}_6\text{H}_4\text{Br}_2$ and LiTePh . Synthesis of the o -Substituted telluro ethers $o\text{-C}_6\text{H}_4(\text{TeMe})_Y$ ($Y = \text{NMe}_2$,

PMe₂, AsMe₂, SbMe₂, OMe, SMe, SeMe and Cl) are also reported. The compounds have been characterized by mass spectroscopy by multinuclear NMR spectroscopy (¹H, ¹³C, ¹²⁵Te) and by the preparation of derivatives. The trends in the ¹²⁵Te NMR chemical shifts are compared and comparison are also made with the ⁷⁷Se NMR chemical shifts in corresponding seleno ethers convenient synthesis for *o*-C₆H₄Cl (SMe) and *o*-C₆H₄Cl (SeMe) are reported⁷⁶.

The chloro (phenyl) trimethane selenourea Te(II) compounds were prepared in 69% yield by treating diphenylditelluride with trimethylene selenourea and chlorine in MeOH. The structure of this and bromo (phenyl) trimethne thiourea Te(II) were determined by x-ray crystallography⁷⁷.

Three coordinated Te(II) complexes of type (*p*-RC₆H₄Te-CH₂ NCSNHN = CR¹R²) Cl (R = H, OH, MeO, R¹ = Ph, C₆H₄OH, R² = H, Me) were prepared by treating *p*-RC₆H₄TeCl₃ with H₂NCSNHN = CR¹R² in aq.MeOH molecular weight and conductivity measurement suggest that the Cl in these complexes is ionic. The I.R., ¹H and ¹³C NMR data suggests that coordination of H₂NCS-NHN = CR¹R² is through S alone, probably giving three coordinates Te. The nature of Te-S bonding and the stability of complexes is reported⁷⁸.

Diarylditellurium *p*-RO-C₆H₄Te-TeC₆H₄OR-*p*(R = Me, Et) react with thiocyanogen in dry absorbtion MeOH at 110°C to give unstable monoaryl Te (II)thiocyanate which were isolated as adducts with neutral M⁺O⁻, OS⁻ donor ligands for example thiourea, β-picoline, triphenylarsene oxide reaction of

diarylditellurium with ICl , IBr gave $p\text{-ROC}_6\text{H}_4\text{TeX}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$)⁷⁹.

$\text{Te}(\text{S}_2\text{COEt})\text{X}$ have been synthesised by $\text{Te}(\text{S}_2\text{COEt})_2$ with TeCl_4 , CuCl_2 or CuBr_2 . The X-ray crystal structure of $\text{Te}(\text{S}_2\text{COEt})\text{Br}$ shows. It is composed of left and right handed helices formed from common sharing (B_1 bridges) of planar $\text{Te}(\text{S}_2\text{COEt})\text{Br}$ units. The C-O bond length is the shortest so far observed in metal xanthates⁸⁰.

The IR and Raman spectra of crystal samples of halo (ethylene thio-urea) phenyl tellurium(II) (halo = Cl, Br, I), halo (ethylene selenourea) phenyl tellurium (II) halo-Cl, Br, phenyldithiocyanato and phenyldiselenocyanato tellurate(II) ions, were recorded below 500 cm^{-1} . From these data, the two fundamental stretching frequencies connected with the approximate linear X-Te-Y linkage were assigned. These frequencies were compared with those obtained from a simplified force constants⁸¹.

The porphyrin Fig.(17) was prepared from 2, 5-bis (phenylhydroxy methyl)tellurophene by reaction with pyrrole followed by cyclocondensation reaction with 2, 5-bis (phenylhydroxy methyl) thiophene⁸².

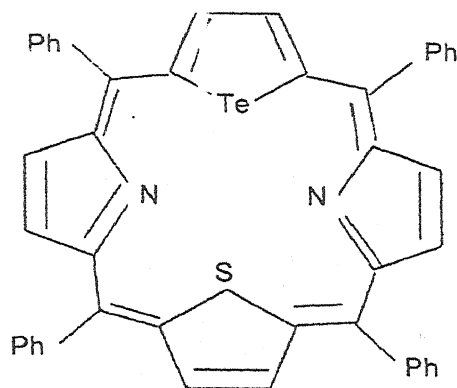


Fig. 17

Successful reduction of benzene derivatives $p\text{-Cl}_3\text{TeC}_6\text{H}_4\text{R}$ ($\text{R}=\text{SiMe}_3$) with $\text{Na}_2\text{S}_2\text{O}_5$ and Cu affords ditelluride $p\text{-RC}_6\text{H}_4\text{Te}_2\text{C}_6\text{H}_4\text{R}$ - p and telluride $(p\text{-RC}_6\text{H}_4)_2\text{Te}$ respectively. Reactions of $p\text{-RC}_6\text{H}_4\text{TeC}_6\text{H}_4\text{R}$ - p and $(p\text{-RC}_6\text{H}_4)_2\text{Te}$ ($\text{R}=\text{SiMe}_3$) with halogens results in oxidation of Te and the formation of the corresponding σ -telluranes. Alkylation of ditellurophenolates anion following upon reduction of RTeCl_3 furnishes p -bis (alkyltelluryl) benzenes⁸³.

The ^{125}Te Mossbauer spectra for $(\text{CF}_3)_2\text{Te}$ and $(\text{C}_6\text{F}_5)_2\text{Te}$ exhibit significantly larger quadrupole splittings than those of Me_2 and $\text{Ph}_2\text{Te}(\text{CF}_3)_2\text{TeX}_2$ and $(\text{C}_6\text{F}_5)_2\text{TeX}_2$ ($\text{X}=\text{F}, \text{Cl}, \text{Br}$) have consistently smaller quadrupole splittings than Me_2TeX_2 and Ph_2TeX_2 . These observations are consistent with the greater electronegativity of CF_3 and C_6F_5 ligands. The ^{125}Te NMR chemical shifts of $(\text{C}_6\text{F}_5)_2$ and its dihalides show a consistent trend to more positive values (increased deshielding as the electronegativity of the ligands attached to Te increases), however, for $(\text{CF}_3)_2\text{Te}$ and its dihalides a more complex pattern is observed which is explained by changes in the mean electronic excitation term in the Ramsay paramagnetic shielding term⁸⁴.

^{125}Te NMR spectra of $\text{Te}(\text{II})$ complexes contained dithiolene on others unsaturated-1, 1-dithio-1, 1-thioseleno or 1, 1-diseleno ligands are reported. According to their chemical shift value, the complexes can be divided into groups will separated by several hundred ppm⁸⁵.

^{125}Te chemical shifts of $\text{Te}(\text{S}_2)_2\text{Te}(\text{NR}_2)_4$ ($\text{R}=\text{Et}, \text{CHMe}_2, \text{iso-BuPhCH}_2$),

$(R_2N=N\text{-pyrrolyl})$ and $Te(S_2CNEt_2)_2X$ ($X = Cl, Br, I, NCS$) are separated by ~ 1400 ppm. When R is an alkyl group, the electronic configuration as contribution to the chemical shift appear to be very small for both oxidation states of Te . The chemical shift of these compounds display a positive temperature dependence consistent with the major contribution arising from paramagnetic shielding. The preparation of $Te(S_2CNEt_2)_2$ from $Te(Et_2NCS)_2$ and that of $Te(S_2CNEt_2)_3I$ from $Te(S_2CNEt_2)_3Cl$ and KI are reported addition of $[(Me_2CH)_2NCS]_2$ and $(Et_2NCS)_2$ to $Te(S_2CNEt_2)_2$ and $CdCl_2$ gave mixture $Te(S_2CNEt_2)_2[S_2CN(CHMe_2)_2]_{4-n}$ ($n = 0-4$), $Te(S_2CNR_2)_4$ disproportionate to $Te(S_2CNR_2)_2$ and $(R_2NCS)_2$ ⁸⁶.

The nature of the bonding to Te in the phosphine complexes R_3PTe and $(R_3P)_2Te$ and in tellurocyanates, $TeCN^-$, $ArTeCN^-$, $ArCH_2TeCN$ and $ArTe(X)CN$ ($X = Cl, Br, I$) was studied by ^{125}Te solution NMR spectroscopy at ambient temperature and by ^{125}Te mossbauer spectroscopy at 4.2K. No evidence was found for multiple bonding to Te in either solution or the solid state. The phosphine complexes R_3PTe give ^{125}Te NMR shifts of -837, -497 ppm (Me_3Te) at ^{125}Te quadrupole splitting of 10-12 mmS⁻¹. The $TeCl^-$ ion has a ^{125}Te NMR shift of -509 to -569 ppm dependent on solvent and conversion, $ArTeCN$ and $ArCH_2TeCN$ shifts of +570-580 ppm and the halide derivative $ArCH_2Te(X)CN^-$, shifts of -586 to 604 ppm Te . ^{125}Te mossbauer quadrupole splitting of $TeCN^-$ is 12 mmS⁻¹ of $ArTeCN$ and $ArCH_2TeCN$ is 13.7-14.1 mmS⁻¹ of $ArCH_2Te(X)CN$, $X=Cl$, is 14.5 mmS⁻¹, $ArCH_2Te(X)CN$, $X = Br$, is 13.8 mmS⁻¹ and $ArCH_2Te(X)CN$, $X = I$ is 14.0 mmS⁻¹⁸⁷.

The chloro and bromophenyl (tetramethylthiourea) tellurium (II) are monoclinic, space group $P_{21/n}$ $z = 4$ chlorophenyl (tetramethylthiourea) Te (II) has $a = 7.7301$, $b = 12.6097$ (8), $c = 15.2179$ (9) Å and $\beta = 99.011$ (6)° $R = 0.040$ bromophenyl (tetramethylthiourea) Te(II) has $a = 7.7306$ (b), $b = 12.8673$ (h), $c = 15.4239$ (II) Å and $\beta = 99.737$ (8)° $R = 0.044$ chlorophenyl (trimorpholinephosphine selenide). Tellurium (II) has $a = 9.2467$ (12), $b = 18.9217$ (16), $c = 13.396$ (12) Å and $\beta = 99.852$ (9)° $R = 0.037$. The first two compounds are isomorphous as are also the last two, the fourth complexes are 3 coordinated T- shaped. In a direction nearly perpendicular to Te-C bond. Te is bonded to halogen atom and in transposition to the halogen atom to a tetramethyl thiourea S on a trimorpholyphosphine selenide Se atom. The three centre systems X- Te- X where X is halogen, are nearly linear and At coordinates, bond angles and bond lengths are reported⁸⁸.

The bis(2-hydroxyethyl) dithiocarbamate tellurium (II) i.e., $\text{Te}(\text{C}_5\text{H}_{10}\text{NO}_2\text{S}_2)_2$ is monoclinic space group $P21/C$ with $a = 11.303$ (S), $b = 5.543$ (1), $c = 28.724$ (5) Å and $\beta = 100.30$ (1)° $D_m = 1.76$ $D_{sc} = 1.83$ mgm^{-3} d (experimental) = 1.76 and d (calculated) = 1.83 for $z = 4$ final $R = 0.066$ for 1314 unique observed reflections. Each Te atom is bonded to all 4S atoms of the 2 ligands forming an asymmetrical planar complex with Te-S bond distance of 2.527 (7) - 2.793 (8) Å. The molecules are linked in pairs by a short intermolecular contact Te-S (2) of 3.296 (Å)° indicating a tendency towards 5 coordination around Te-two of the four EtOH groups in the molecule show a disorder of orientations⁸⁹.

The tellurium (II) ethyl xanthate with 4,4-bipyridyl is monoclinic space group P21/c with $a = 9.0249(9)$, $b = 13.211(2)$, $c = 14.347(2)$ Å and $\beta = 102.3(2)^\circ$ $d(\text{expt L}) = 1.77$ and $d(\text{calculated}) = 1.780$ for $Z = 4$ final $R = 0.053$. Crystals of the adducts consist of molecular binuclear species. Each of Te had planar pentagonal coordination by 4S from two bidentate xanthate ligands and one of the bipyridine⁹⁰.

The trans bis 2(3H)-benzimidazolethione bis(thiourea) tellurium(II) chloride i.e., $\text{Te}(\text{CH}_4\text{N}_2\text{S})_2(\text{C}_7\text{H}_6\text{N}_2\text{S})_2\text{Cl}_2$ is monoclinic space group Pz1/C with $a = 6.623(1)$, $b = 11.3873(3)$, $c = 16.085(3)$ Å and $Dc = 1.787$ for $z = 2$. The final $R = 0.029$ and $R_w = 0.027$ for 2068 reflections. The Te lying at the crystallography centre of symmetry is bonded to a thiourea 5 atoms and 2 benzimidazole thione 5 system (atoms) in a trans square planar arrangement. The TeS_4 group has the dimensions $\text{Te-S}(1) 2.694(2)$ $\text{Te-S}(2) 2.685(1)$ Å and $\text{S}(1) \text{Å}$ and $\text{S}(1) - \text{Te-S}(2) 89.4(1)^\circ$ ⁹¹.

$\text{Te}(\text{tu})_2(\text{ClO}_4)_2$ (tu = thiourea is triclinic, space group P1 with $a = 15.35$, $b = 11.97$, $c = 6.01$ Å, $\alpha = 90.1$, $\beta = 91.0$ and $\gamma = 108.0^\circ$ $Z = 2$ final $R = 0.032$ $\text{Te}(\text{dmtu})_4\text{Cl}_2$ (dmtu = 1,3-dimethyl thiourea) is monoclinic space group P21/n with $a = 13.70$, $b = 9.05$, $c = 10.91$ Å and $\beta = 101.6^\circ$ $Z = 2$ final $R = 0.025$). In both the complexes the Te is bonded to four S atoms in a planar arrangement which is considerable distorted in the perchlorate but nearly regular in the chloride, to explain the structural and ^{125}Te , mossbauer spectroscopy results a bonding model involving lone pair with S and p characteristics then proposed⁹².

The bromo (o-ethylxanthato) tellurium(II) is monoclinic space group P21/C with $a = 10.636(1)$, $b = 6.030(1)$, $c = 13.364(1) \text{ \AA}$ and $\beta = 103.32(1)^\circ$ $d(\text{expt}) = 2.66$ and $d(\text{calculated}) = 2.617$ for $Z = 4$ final $R = 0.077$ ($R_w = 0.072$) each Te is bonded to 2S atoms of the xanthate ligand and 2 Br atoms with each Br atom bonded to another Te atom. The Te and Br atoms adopt a helical structure with a pairs of Br and Te atoms forming the repeat unit⁹³.

X-ray data for the bis(thiobenzoate-5) tellurium i.e., $\text{C}_{14}\text{H}_{10}\text{O}_2\text{S}_2\text{Te}$ indicate that Te is covalently bonded to S. There are weak secondary interactions between Te and O which complete in S_2O_2 coordination around Te. The CO and CS distances of I are normal and agree with published values. The two pH rings are planar with the C atoms deviating from the plan by less than $0.01(1) \text{ \AA}$. The average CH distance is $0.86(4) \text{ \AA}$ and the average C-C-H angle is $120(7)^\circ$

94.

Te(II) 2-oxazolidinene derivatives are useful as intermediate for drugs of animal and human are prepared by treating olefins with carbamates esters in the presence of Lewis acids and $\text{ArTe}(\text{O})\text{OCR}$ ($\text{Ar} = \text{Un}$) substituted aryl haloalkyl as mediators. Cis 4-octene $\text{H}_2\text{NCOOCF}_3$ and $\text{BF}_3\text{Et}_2\text{O}$ were added to a solution of $\text{PhTe}(\text{O})\text{COOCF}_3$ in dichloroethane and the mixture was refluxed for 12 hours to give 85% cis-4,5-di-n-propyl-1,3-oxazolidine-2-one⁹⁵.

Ethynylepichlorohydrin ($\text{R}^1 = \text{alkyl, H, Ph, tetrahydropyranyloxymethyl}$) were treated with Na_2Te to give telluriophenomethanols⁹⁶.

$\text{O}^-(\text{Me}_3\text{Si})_2\text{C}_6\text{H}_4$ reacted with two equivalent TeCl_4 in $\text{O}-\text{Cl}_2\text{C}_6\text{H}_4$ to give 66% $\text{o}-(\text{Cl}_3\text{Te})_2\text{C}_6\text{H}_4$, which was reduced with $\text{Na}_2\text{S}_2\text{O}_5$ to give the polymeric ditelluride $(\text{o}-\text{C}_6\text{H}_4\text{Te}_2)_n$. Further reduction of $\text{6-C}_6\text{H}_4\text{Te}_2$ with NaBH_4EtOH and cyclization of the resulting di-Na derivative with CH_2Br_2 gave 16% benzoditellurole which gave the tetra bromide with Br^{97} .

The compound fig.18. ($\text{R} = \text{H}$, $\text{M} = \text{M}^1 = \text{Te, Se}$, $\text{R}^1 = p\text{-MeOC}_6\text{H}_4$, $p\text{-EtOC}_6\text{H}_4$, $p\text{-MeC}_6\text{H}_4$, $\text{R} = \text{Me}$, $\text{M} = \text{Te}$, M^1Se , $\text{M} = \text{Se}$, $\text{M}^1 = \text{Se}$, $\text{R}^1 = p\text{-MeO-C}_6\text{H}_4$) via an intermediate singlet benzyne, have been synthesised⁹⁸.

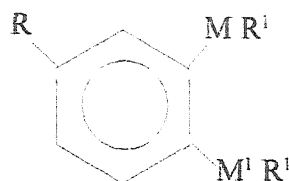


Fig. 18

Mossbauer data are reported for a number of heterocyclic compounds contain Te (Fig.19). The influence of the bulky-2-biphenyl ligand on the mossbauer parameters of diaryltellurium dihalides and aryl tellurium trihalides was also investigated⁹⁹.

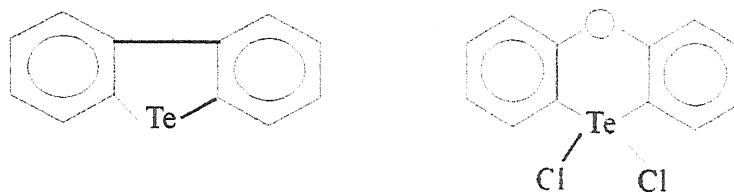


Fig. 19

Elemental Te reacted with C_2H_2 and PhI in $\text{HMPA-H}_2\text{O}$ contained SeCl_2 and KOH in an autoclave 100-120 and 10-12 atoms to give 20% $\text{PhTeCH}=\text{CH}_2(\text{I})$, 17% $(\text{CH}_2=\text{CH})_2\text{Te}$ and 20% Ph_2TeI information was reduced to <1%

with PhBr instead of PhI or in the absence of SnCl_2 and was inhibited by added hydroquinone or with PhCl. . An anion radical mechanism was proposed¹⁰⁰.

Solution of disodium ditelluride in DMF react with the solvent to give small yield of the unusual ditelluride $[\text{Me}_2\text{NC(O)}]_2\text{Te}$. This molecule exhibit interesting photochemical behaviour and was experimentally characterised and its crystal structure was determined¹⁰¹.

XPS (ESCA, electron spectroscopy for chemical analysis) of oxatellurolylium halides Fig.20 (R = halo, R^1 =alkyl, aryl, R^2 =aryl) and dioxatellurapentalenes (same R^1, R^2) have shown them to be Te(II) compounds. When their $\text{Te}3d_{5/2}$ binding energies are compared to those of te(II) models. The oxatellurolylium trihalides (same R^1, R^2) and, by extension, the dioxatellurapentalene dihalides (R = H, Cl) $\text{Te}3d_{5/2}$ binding energies consistent with Te(IV) when compared to te(IV) compounds. Changes in XPS binding energies which result from substituent changes in the carbon framework are similar in magnitude to changes, from substitution in the electronegative ligands attached to Te, this makes quantitative assessment of the effect of higher order bonding on the electronic environment at Te difficult usingh the $\text{Te}3d_{5/2}$ binding energies.

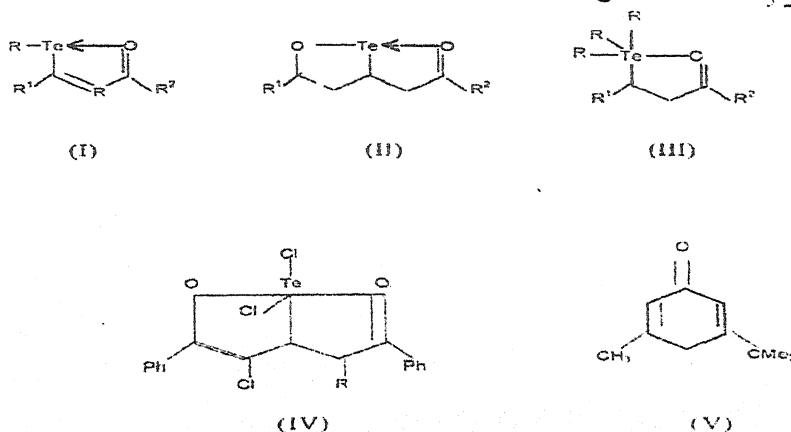


Fig. 20
(28)

The Ols electrons of (I-III) have higher binding energies than model compounds (V) ($X = \text{Te}, \text{TeCl}_2$) suggesting that partial bonding (linear, there is centre four electron bonding) exists between the Te halides. The Te and the one oxygen ($\text{RTe} \dots \text{O}$) while the XPS data show the oxygen atoms to be donating electrons in the $3\text{C}-4\text{e}$ bonds, the ^{125}Te NMR chemical shifts show deshielding as three centre four electron

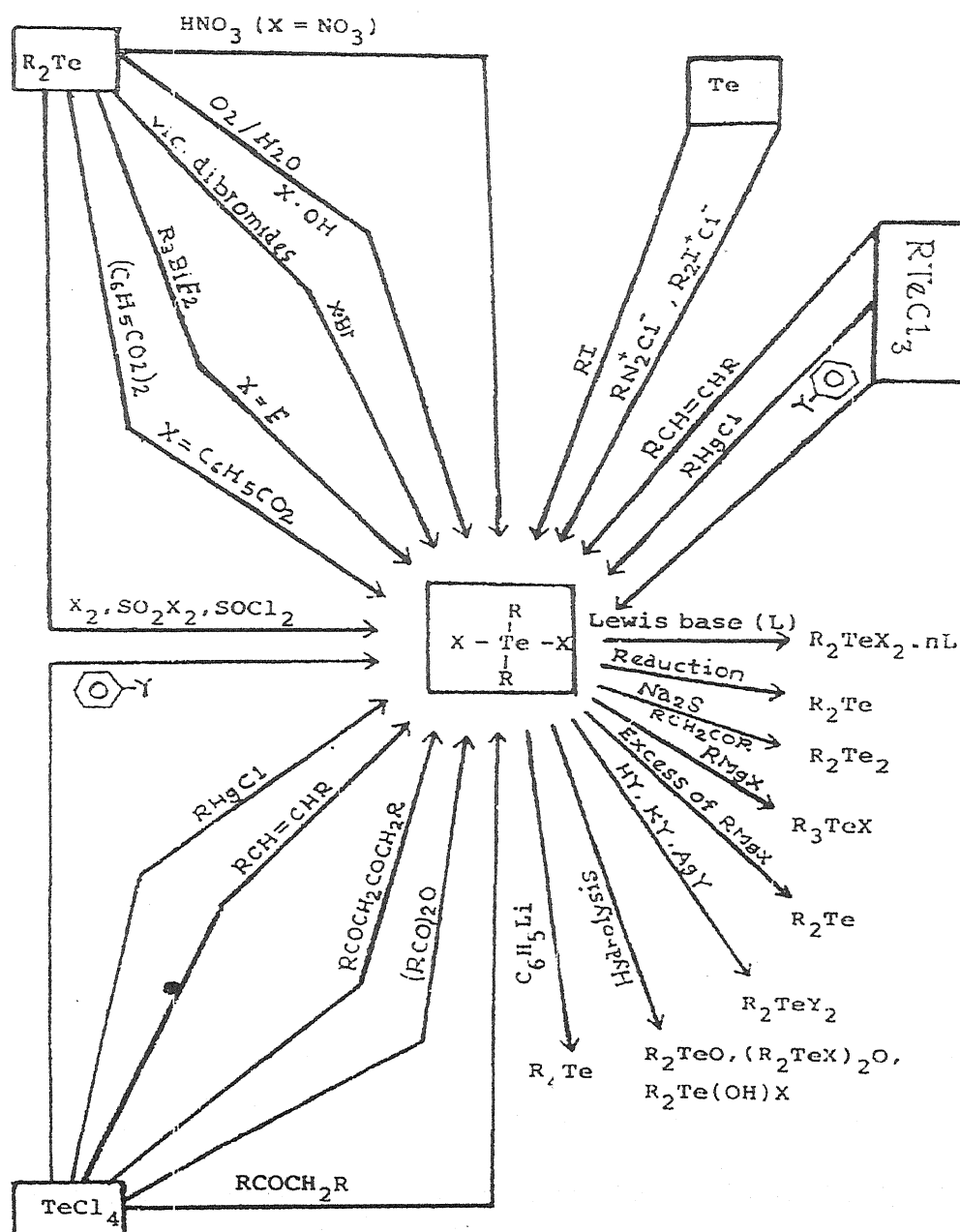


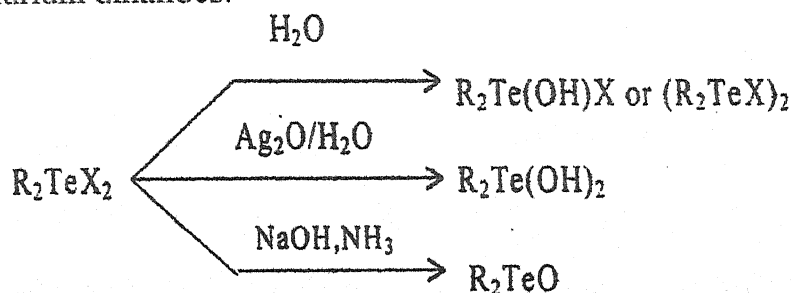
Fig. 21 : Synthesis and reactivity of R_2TeX_2

NMR chemical shifts move subsequently down field from VI to β (tellurophenyl) butenoate ester (I) ($R = \text{Ph}$, $R^1 = \text{Me}$, $R^2 = \text{OEt}$ to (I) ($R = \text{iodo}$ to (I) ($R = \text{Br}$ to (I) ($R = \text{Cl}$) in the Te(II) series and Te(IV) respectively. The XPS and ^{125}Te NMR structure of these compounds are first systematic studies of this type of compounds as, the data suggests that ^{125}Te NMR chemical shift are sensitive to the geometry of the complexes, the oxidation state of Te and electronic environment of Te¹⁰².

(iii) Compounds in oxidation state (IV)

Most common compounds of tellurium have metal in the oxidation state (IV). Organotelluriumtrihalides (RTeX_3), diorganotelluriumdihalides (R_2TeX_2), triorganotellurium halides (R_3TeX), tetraorganotellurium (R_4Te), organotetrahalotellurates $\text{M}^+[\text{RTeX}_4]^-$ and $\text{M}_2[\text{R}_2\text{TeX}_4]$ ^{103,104} and telluroxides (R_2TeO) come under this category.

RTeX_3 , R_2TeX_2 and R_3TeX generally behave as Lewis acids of class 'b'. Organotellurium trihalides and diorganotellurium dihalides on reduction yield R_2Te_2 and R_2Te respectively. The hydrolysis product of aryltellurium trihalides is tellurinic acid halide, RTe(O)X , in which tellurium atom is tetracoordinated in a trigonal bipyramidal structure. The following scheme describes the hydrolysis of diorganotellurium dihalides:



The reactivity of organotellurium trihalides when they condense with activated organic compounds with the formation of hydrogen halide and bis(organo) tellurium dihalides decrease in the order $\text{Cl} > \text{Br} > \text{I}$. RTeX_3 react with various organometallic derivatives of Hg, Sn, Pb, Si, Ga, In and Tl yielding R_2TeX_2 and their organometallic derivatives. Synthesis and reactivity of dihalides and trihalides are summarized in (figures.21 and 22) respectively.

On the basis of X-ray determination, R_2TeX_2 derivatives have been assigned a structure shown in Fig.23^{105,108}.

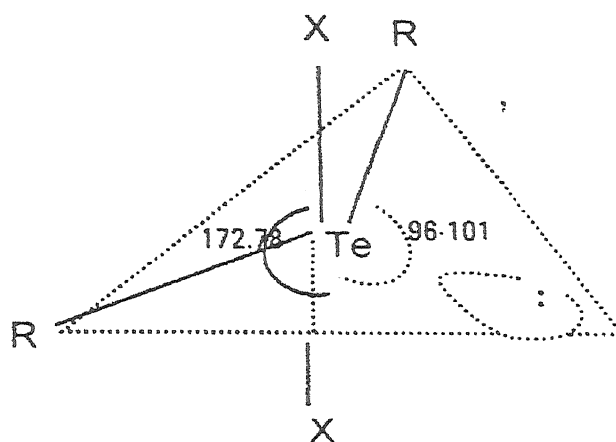


Fig. 23 Structure of trigonal bipyramidal

The tetrakis (dialkyl dithiocarbamato) tellurium(IV) are highly effective. Thermal antioxidants and melt stabilizers for polypropylene and converted to the bis(dialkyl dithiacarbamato) tellurium(II) complexes¹⁰⁹.

$\text{Me}_2\text{Te}(\text{S}_2\text{COR})_2$ ($\text{R} = \text{Me}, \text{Et}, \text{Me}_2\text{CH}$) are obtained by reaction of Me_2TeI_2 with freshly prepared sodium xanthates. Another preparative method is the insertion of CS_2 into dimethyl tellurium bis(alkoxides). The X-ray analysis of

$\text{Me}_2\text{Te}(\text{S}_2\text{COMe})_2$ shows that in the crystals the molecule has a four configuration around Te^{110} .

$\text{TeX}_4\cdot\text{L}$ ($\text{X} = \text{Br}, \text{Cl}, \text{L} = \text{tetramethyl and tetraethyl dithioxamides}$) were prepared by the addition of $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$ solutions of TeX_4 to the ligands. The adducts were characterized by IR and UV spectra. The spectral measurements suggest octahedral structure with coordination through the S atoms. However, the distinction between bridging or bidentate moieties could not be made¹¹¹.

Reactions of PhTeCl_3 with $(\text{S}_2\text{CNEt}_2)$, $(\text{S}_2\text{P}(\text{OEt})_2)^-$ and $(\text{S}_2\text{COEt})^-$ in solution were studied by variable temperature ^{125}Te , ^{31}P , and ^{13}C NMR spectroscopy which show the formation of a variety of mixed ligand species; some of which were subsequently isolated. $\text{MeTe}(\text{I})(\text{S}_2\text{CNEt}_2)(\text{I})$ formed by oxidative addition of MeI to $\text{Te}(\text{S}_2\text{CNEt}_2)_2$ also provides a useful way to the synthesis of mixed ligand species, but in general the products are less stable than the pH analogous. Solvent dependent intramolecular exchange processes were observed for the alkyl and aryl series. The crystal and molecular structure of all mixed ligand complexes and $\text{PhTe}(\text{S}_2\text{CEt}_2)(\text{S}_2\text{P}(\text{OEt})_2)$ have been also determined¹¹².

$\text{Ph}_2\text{Te}(\text{S}_2(\text{COR}))_2$ and telluracyclopentane-1, 1-bis(alkyl xantahates) ($\text{R} = \text{Me}, \text{Et}, \text{CHMe}_2$) are obtained by reaction of Ph_2TeCl_2 or tellura cyclopentane-1, 1-diiodide with ROCH_2Na . The insertion of CS_2 into organotellurium bis(alkoxides) is only successful in the case of the cyclic compounds. The prod-

ucts decomposition on heating to Ph_2Te or telluracyclopentane and $\text{ROCS}_2\text{S}_2\text{COR}$ ¹¹³.

$\text{R}_2\text{Te}(\text{S}_2\text{CNR}_2^1)_2$ ($\text{R} = \text{Me, Ph, R}^1 = \text{Me, Et, CHMe}_2, \text{cyclohexyl, Ph}$) were prepared from Me_2TeI_2 or Ph_2TeCl_2 and $\text{R}_2^1\text{NCS}_2\text{Na}$ from R_2^1NH , CS_2 and Me_2TeI_2 or Ph_2TeCl_2 by several other methods. Products of Me_2TeI_2 with $\text{NaS}_2\text{CNMeCH}_2\text{CH}_2\text{NMeCS}_2\text{Na}$ were obtained as polymers. Decomposition of $\text{R}_2\text{Te}(\text{S}_2\text{NR}^1)_2$ gave R_2Te , $\text{R}_2^1\text{NCS}_2\text{S}_2\text{CNR}^1_2$ and other products¹¹⁴.

Ph_3TeOR ($\text{R} = \text{Me, Et, CHMe}_2, \text{}$) were obtained by treating Ph_3TeCl with RONa-ROH . $\text{Ph}_3\text{TeS}_2\text{COR}$ were obtained from Ph_3TeCl and NaS_2COR from $\text{Ph}_3\text{Te OR}$ and CS_2 , $\text{Ph}_2\text{TeS}_2\text{CSR}$ were prepared from Ph_3TeCl and NaS_2CSR ¹¹⁵.

Preparation and structural aspects of perchlorate complexes of Te(IV) with $\text{RR}^1\text{NCS}_2^-$ ($\text{R} = \text{R}^1 = \text{Me, Et, Ph, CHMe}_2$, $\text{PR}^1\text{N} = \text{piperideno morpholino}$) are reported¹¹⁶.

A number of dithiocarbamate derivatives $\text{Ph}_2\text{Te}(\text{S}_2\text{CNR}_2)_2$ ($\text{R} = \text{Me, Et}$) and $\text{Ph}_2\text{TeCl}(\text{S}_2\text{CMR}_2)$ ($\text{R} = \text{Me, Et, CHMe}_2$) were prepared and characterised initially by analysis and vibrational spectroscopy. The crystal structures were determined so that the effect of the change in the nature of R and the presence of a Cl atom could be compared. The dithiocarbamate groups are monodentate (or anisobidentate) and the geometry about Te is consistently that of a dis-

torted sawhorse structure. Examples of both inter and intramolecular Te-S interactions are observed as well as an intermolecular Te-Cl interaction. The crystal structure of (R = Me) and (R = Et, CHMe₂) were determined. NMR spectra are not simple and indicate that several species are present in solution¹¹⁷.

Ph₂TeS₂CNR₂ (R = Me, CHMe₂Ph) were prepared on heating Ph₃TeCl with R₂NCS₂Na. Ph₃TeS₂CNMe, CH₂CH₂NMeCS₂TePh₃ was similarly prepared. Ph₃TeS₂CNR₂ (R = Me) was also obtained from Ph₃TeO₂CNMe₂ and CS₂ thermal decomposition of Ph₃TeS₂CNR₂ gave R₂NCS₂Ph and Ph₂Te¹¹⁸.

RTeX₂[S₂P(OR¹)₂] and R₂Te [S₂P-(OR¹)₂]₂ (R = *p*-MeOC₆H₄, Ph, R = Me, Et, CHMe₂; X = Cl, Br) were prepared in 56-57% yields from the NH₄⁺ and Na salts of dithiophosphoric acid and the appropriate aryl tellurium trihalide or diaryl tellurium dichloride in CS₂ and were characterized by elemental analysis with proton NMR, I.R. and Raman spectra¹¹⁹.

The crystal structure of [*p*-MeOC₆H₄TeBr₂(S₂P(OMe)₂)] and Ph₂Te[S₂P(OMe)₂]₂ were determined in [*p*-MeOC₆H₄TeBr₂.S₂P(OMe)₂]. The dithiophosphate group is bidentate while in [Ph₂Te S₂P(OMe)₂]₂ it is monodentate in first compound the geometry around Te is that of a distorted square pyramidal, whereas in second compound it is that of a distorted sawhorse structure. In both cases a distorted octahedral confirmation about Te is completed¹²⁰.

TeCl_4L_2 (L = substituted thiourea) were prepared and characterized by elemental analysis, electrical conductivity, thermal analysis, I.R. and NMR spectral methods. The complexes are octahedral monomers with S-coordinated ligand¹²¹.

Diphenyl selenium(IV) bis(O, O'-dialkyl dithiophosphates) $\text{Ph}_2\text{SeS}_2\text{P(OR)}_2$ (R = Et, CHMe_2 , CH_2CHMe_2) diphenyl selenium(IV) bis(O, O'-alkylene dithiophosphates) $\text{Ph}_2\text{Se(S}_2\text{POR''O)}_2$ (R'' = $\text{CH}_2\text{CMe}_2\text{CH}_2$, $\text{CHMeCH}_2\text{CMe}_2$), $\text{PhTe[S}_2\text{P(OCHMe}_2\text{)]}_3$ and organotellurium(IV) tris(O, O'-alkylene dithiophosphates) $\text{RTe(S}_2\text{POR''O)}_3$ (R = Ph, p-MeOC₆H₄, R = $\text{CH}_2\text{CMe}_2\text{CH}_2$) have been prepared and characterized from physicochemical and spectral (IR, ¹H and ³¹PNMR) studies. The results indicate a pseudotrigonal bipyramidal geometry around the selenium atom where the four position are accepted by the two Ph and two dithiophosphate ligands and the remaining one vacant position is occupied by a lone pair of electrons¹²².

In the reaction of 3,3-bis (chloromercuric-2, 4-pentane dione [(HgCl)₂L]) with TeCl_4Ph_2 or Ph_3TeCl replacement of one HgCl group by a Te moiety gives $\text{Cl}_3\text{TeLHgCl}_2\cdot\text{C}_4\text{H}_8\text{O}_2\cdot\text{Ph}_2\text{Te(Cl)LHgCl}$ and $\text{Ph}_3\text{TeLHgCl}$ respectively. The I.R. and ¹H NMR data indicate that Te is bonded to C₃ carbon of acetyl acetone. In solution the compounds appear to ionize into Cl⁻ and an organometallic cation in which Hg seems to be involved in second interaction with the carbonyl groups. Far I.R. and mass spectral data suggest that Hg-O interaction is significant in solid structure or state¹²³.

The complexes $[R_2Te(p-OC_6H_4CHO)_2]$ ($R = Ph, Me, p-eOC_6H_4$, biphenylene) have been prepared by the reaction of $R_2Te(OMe)_2$ with salicylaldehyde. It reacts with haloacetic acid R^1COOH ($R^1 = CF_3, CCl_3, CHCl_2, CH_2Cl$) to give mixed ligand complexes $[R_2Te(p-OC_6H_4CHO)O_2CR^1)]^{124}$.

$Ph_3Te(RCOH;CR^1O)$ ($R = Me, Ph, CF_3$, $R^1 = Me, Ph, CF_3, 2\text{-thienyl}$) were prepared. The I.R., 1H and ^{13}C NMR and mass spectra were discussed in conjunction with molecular weight and constant data, weak coordination of the diketone to the Te atom is common structural feature¹²⁵.

The reaction of (AcAc) with $RTeCl_3$, R_2TeCl_2 and R_3TeCl ($R = Ph, 4-HOC_6H_4, 4-MeOC_6H_4, 4-EtOC_6H_4, 3-Me-4-HOC_6H_3, 3,4-(HO)_2C_6H_3$), have been investigated. $RTeCl_3$ gives $RTe(C_5H_4O_2)$ type derivatives but $RTeCl_2$ and R_3TeCl do not react even on prolonged refluxing in the presence of anhydrous $AlCl_3$. The structural features of the new acetyl acetone derivatives $RTe(C_5H_4O_2)Cl_2$ have been explored by I. R., NMR spectroscopy. The effect of phenyl ring substitution of the keto-enol tautomerism of $RTe(C_5H_4O_2)Cl_2$ has been found to be minor. The bond formation between Te and C-1 of AcAc and intramolecular secondary interaction between the oxygen of AcAc and Te have been obtained from the spectral data¹²⁶.

Diorganotellurium (IV) bis (β -diketonates) of the formula $R_2Te(acacH)_2$ ($R = CH_3, C_6H_5, p-CH_3OC_6H_4$) ($acacH = 2,4$ pentanedione) and $R_2Te(dpm)_2$ ($dpmH = 2,2,6,6$ -tetramethyl heptane-3,5-dione) have been prepared by the

reaction of $R_2Te(OMe)_2$ with (acacH) and (dpmH) in anhydrous condition. $R_2Te(acac)_2$ reacts with halocarboxylic acid ($R'COOH$) ($R' = CF_3, CCl_3, CHCl_2, CH_2Cl$) to give mixed ligand compound of the type $R_2Te(acac)(R'COO)$. A weak coordination of the β -diketone group with tellurium atom in solid state is concluded. The geometry around the central tellurium atom is suggested in the basis of physicochemical studies¹²⁷.

Tellurium dioxide trimethyl chlorosilane, acetyl chloride or acetyl bromide in glacial acetic acid generated a homogeneous solution. Addition of cyclohexene produced trans-2-halocyclohexyl tellurium trihalides of excellent purity in 70% yield with dichloromethane or ethanol free chloroform. The same compounds hence obtained from heterogeneous reaction mixture, trans 2-methoxycyclohexyl tellurium trihalide was obtained from tellurium dioxide, trimethylchlorosilane and cyclohexene in absolute methanol. In the absence of cyclohexene $TeCl_4$ was obtained in 91% yield from tellurium dioxide and trimethylchlorosilane in $CHCl_3$ and $TeBr_4$ in 98% yield from tellurium dioxide and acetyl bromide in glacial acetic acid¹²⁸.

Reactions of aryltellurium (IV), chlorides $ArTeCl_3$ and Ar_3TeCl ($Ar = ph, 4-MeOC_6H_4, 4-HOC_6H_4, 3-MeO-4-HOC_6H_3, 2,4-(HO)_2C_6H_3, 3,3-bis(chloromercuryl)-2,4-pentandione$ and several β diketones and their sodium salts)¹²⁹.

The I.R. spectra of twenty four diaryltellurium dicarboxylates are re-

ported. The main bonds in the I.R. are tentatively assigned and their frequency values compared to those data of related compounds. The trigonal bipyramidal arrangement is proposed as the more likely structure for these compounds¹³⁰.

NMR chemical shifts, dipole moments and pka values were determined for $\text{RC}_6\text{H}_4\text{TeX}_2\text{C}_6\text{H}_4\text{NMe}_2$ -4 ($\text{R} = 4\text{-Me}_2\text{N}, 4\text{-MeO}, 4\text{-EtO}, 4\text{-PhO}, 4\text{-Me}, \text{H}, 4\text{-H}, 4\text{-Br}, 3\text{-Br}, \text{X} = \text{Cl}, \text{Br}, \text{I}$). The pka values were correlated with substitution constant for $\text{RC}_6\text{H}_4\text{TeX}_2\text{C}_6\text{H}_4\text{NMe}_2$ -4 ($\text{X} = \text{Cl}, \text{Br}$), electronic effects were transmitted more poorly through TeCl_2 and TeBr_2 groups than through Te by factors of 2.31 and 3.10 respectively. Transmission factors were also observed for the $\text{C}_6\text{H}_4\text{TeCl}_2$ and $\text{C}_6\text{H}_4\text{TeBr}_2$ group.¹³¹

Comparison of calculated and experimental dipole moments of $(\text{RC}_6\text{H}_4)_2\text{Te}_2$ ($\text{R} = \text{H}, 4\text{-Me}, 4\text{-MeO}, 4\text{-EtO}, 4\text{-Cl}, 4\text{-Br}, 3\text{-Cl}, 3\text{-Br}$) indicated that in benzene $(\text{RC}_6\text{H}_4)_2\text{Te}_2$ exist in the gauche form with dihedral angle of 75° . The effect of including d orbitals of Te in the calculations of the total energy of ditellurides was reported. Rotational barrier for MeX_2Me ($\text{X} = \text{S}, \text{Se}, \text{Te}$) were calculated by the extended Huckel method. The most stable conformation of MeX_2Me was very similar to that of $(\text{RC}_6\text{H}_4)_2\text{Te}_2$ ¹³².

Diphenylene tellurium (IV) dichloride was prepared and its interaction with various silver salts (Ag^+X^-) donor bases (L) and R_4NCl have been studied. Its reduction products diphenylene te (II) undergoes oxidative addition with halogens and interhalogen. It also acts as a Lewis base forming molecular adducts with strong acceptors such as HgCl_2 . A few organic tellurium derivatives

show appreciable antiviral activity¹³³.

$(\text{PhCH}_2)_2\text{TeX}_2$ ($\text{X} = \text{iodo, cyano, thiocyanato, IO}_3, \text{NO}_3, \text{pyridine, morpholine, piperidine}$) were prepared and characterized. These compounds are finally or fairly stable. The antibacterial activity indicated that compounds with Te (II) oxidation state possess antibacterial activity comparable to that of tetracycline those of Te(IV) are inactive¹³⁴.

RTeCl_3 ($\text{R} = \text{Ph, 4-MeOC}_6\text{H}_4, \text{6-PhOC}_6\text{H}_4$) reacted with $\text{Me}_3\text{SiNR}^1\text{R}^2$ [$\text{R}^1 = \text{R}^2 = \text{Et, R}^1\text{R}^2 = (\text{CH}_2)_4$] under dry nitrogen atmosphere to give $(\text{R}^1\text{R}^2\text{N})\text{TeCl}_2$ and Me_3SiCl . The products decomposed to give $(\text{R}^1\text{R}^2\text{NH}_2)^-(\text{RTeCl}_4)^+$. R_2TeCl_2 did not react with $\text{Me}_3\text{SiR}^1\text{R}^2$ even on refluxing for 6 hours. R_2TeCl_2 was reduced by Et_2NLi to give R_2Te ¹³⁵.

Coordinative interaction between TeCl_4 or RTeCl_3 ($\text{R} = \text{aryl}$) and transition metal chelates of the general formula: $\text{R}_n\text{TeCl}_{4-n}\text{M}$ ($n = 0 \text{ or } 1$) [$(\text{R} = \text{Ph, } p\text{-MeOC}_6\text{H}_4, \text{EtOC}_6\text{H}_4, \text{M} = \text{Ni(II)})$] $\text{LH}_2 = \text{Schiff-bases derived from salicylaldehyde or o-hydroxy acetophenone}$ on the complexes in solid state indicate coordination of the metal chelates to Te (IV) via 2-phenolic O atoms, planarity about the transition metal ions is thus retained¹³⁶.

$\text{Te}(\text{CH}_2\text{CH}_2\text{Ph})_2$ was prepared by alkylation of Na_2Te with the corresponding alkyl bromide. The resulting slightly air sensitive which can be converted to a stable diiodide and forms stable coordination complexes with PdCl_2 and PtCl_2 . The geometry of these complexes $\text{MCl}_2[\text{Te}(\text{CH}_2\text{CH}_2\text{Ph})_2]_2$ ($\text{M} = \text{Pd, Pt}$),

Pt) were studied by far I.R and Raman spectroscopy. The Pt complexes was also studied by ^{125}Te NMR spectroscopy, a useful probe for observing cis-trans isomerization in such complexes and the first Te-Metal coupling constant for such complexes are reported ($\text{JTe}^{125}\text{-Pt}^{195}$ cis 900 HZ trans 544 HZ)¹³⁷.

Treating Ph_2TeO with strong lewis acid SnCl_4 , TiCl_4 and SbCl_5 gave 75-80% Ph_2TeCl_2 whereas RTeCl_3 ($\text{R}=\text{Me}$, $p\text{-MeOC}_6\text{H}_4$, $p\text{-PhOC}_6\text{H}_4$) gave RTeCl_3 , Ph_2TeO . The I.R. spectra of ($p\text{-R}^1\text{C}_6\text{H}_4$) $_2\text{TeO}$ ($\text{R}^1=\text{H}$, MeO) Were studied¹³⁸.

Some aryl tellurium (IV) compounds (e.g., $p\text{-MeOC}_6\text{H}_4\text{TeCl}_3$) react with iodine and bromine to give the corresponding aryl halides (e.g., $p\text{-MeOC}_6\text{H}_4\text{I}$) in good to moderate yields (iodo and bromoditelluration). The addition of NH_4F , CsF , KF , SbCl_5 and HgCl_2 accelerates the reaction in some cases compared to these haloditellurium, chloroditelluration and cyanoditelluraion of these compounds were very sluggish¹³⁹.

Twenty five $p\text{-RC}_6\text{H}_4\text{TeCl}_3\text{L}$ ($\text{R}=\text{MeO}$, PhO ; $\text{L}=\text{N-}$, O- and S-donor Lewis bases e.g., Et_2N , Ph_3PO , Me_2SO) were prepared by treating RTeCl_3 with L in CH_2Cl_2 . They were screened for their antibacterial and antifungal activities¹⁴⁰.

Reaction of Ph_2TeCl_2 on $p\text{-EtOC}_6\text{H}_4\text{TeCl}_3$ with donor ligands for example, pyridine, DMF, Me_2SO , Ph_3ps etc. gave 1:1 complexes. A few of the complexes showed activity against gram negative bacteria. All of the com-

pounds were completely inactive towards pathogenic fungi¹⁴¹.

RTeCl_3 ($\text{R} = 4\text{-MeOC}_6\text{H}_4$, $4\text{-HOC}_6\text{H}_4$) reacted with $(\text{R}^1_4\text{N})\text{X}$ ($\text{R}^1 = \text{Me, Et, Ph, Bu}$ $\text{X} = \text{Cl, Br, I}$) to give $(\text{R}^1_4\text{N}(\text{RTeCl}_3\text{X}))$ ($\text{X} = \text{SCN, iodo}$) were also prepared. The fungicidal and bactericidal activity of RTeCl_3 was affected by complexation¹⁴².

Treatment of mercaptan to azines with Te(IV) halides in dioxanes THF or Me_2CHOH gave 2:1 adducts configuration, the thione tautomer of the heterocycles, e.g. treatment of 1-methyl-2 imidazolethiol with TeCl_4 in dioxane gave 93% of the 2;1 adduct $(\text{TeCl}_4\text{L}_2)$ dioxane ($\text{L} = 1\text{-methylimidazole-2(3H)thione}$). The Te (IV) ion in the adducts has a sterically inert lone pair and thus a pseudooctahedral coordinations¹⁴³.

Condensation of TeF_4 or TeCl_4 with Me_3SiNR_2 ($\text{NR}_2 = \text{Et}_2\text{N, morpholine, piperidine}$) in C_6H_4 gave 46-94% $(\text{R}_2\text{N})_2\text{TeX}_2$ ($\text{X} = \text{F, Cl}$). Treatment of $(\text{R}_2\text{N})_2\text{TeF}_2$ ($\text{R}_2\text{N} = \text{morpholine}$) with $(\text{Me}_3\text{S})_2\text{NSO}_3\text{C}_6\text{H}_4\text{P}^1\text{-4}$ ($\text{P}^1 = \text{H, Me}$) gave $(\text{R}_2\text{N})_2\text{TeNSO}_2\text{C}_6\text{H}_4\text{R}^1\text{-4}$ ¹⁴⁴.

$\text{RC}_6\text{H}_4\text{TeCl}_3$ ($\text{R} = 4\text{-Me, H, 4-MeO, 4-EtO, 4-PhO, 4-Cl, 4-Br, 3-Cl, 3-Br, 3-O}_2\text{N}$) reacted with $4\text{-AcOHgC}_6\text{H}_4\text{NMe}_2$ in refluxing dioxane to give $\text{RC}_6\text{H}_4\text{TeCl}_2\text{C}_6\text{H}_4\text{-NMe}_2\text{-4}$. The dipole moments increased in the state order R and their basicity constants decrease in approximate, the same order A correlation analysis indicated transmission coefficient of 0.16 and 0.54 for the $\text{C}_6\text{H}_4\text{Te}$

and Te bridging groups respectively¹⁴⁵.

$\text{Ph}_2\text{Te}(\text{O}_2\text{CCF}_3)_2$ forms 1:1 molecular adducts with various N,O and S donor basis. The corresponding reactions with $\text{Ph}_2\text{Te}(\text{O}_2\text{CCCl}_3)_2$ depend upon the nature of the bases. $\text{Ph}_2\text{Te}(\text{O}_2\text{CCCl}_3)_2$ give 1:1 molecular adducts with diethyl acetamide and morpholine (whereas the 4picoline, tetramethyl piperidine and dimethyl acetamide ligands L afford $(\text{Ph}_2\text{TeCl}_2\text{L})$ with 3-picoline-M-oxide (L^1) and Cl^- and $(\text{Ph}_2\text{Te}(\text{CCl}_3)_2\text{L}^1)$ and $(\text{Ph}_2\text{Te}(\text{CCl}_3)_2\text{Cl})^-$ respectively are obtained¹⁴⁶.

The reaction of bis (benzoyl) tellurides with primary or secondary amines or potassium ethanoiate yield the corresponding tellurobenzoic acid salts, which are readily oxidized with iodine or benzene sulfonylurea chloride is afford novel bis (benzoyl) ditelluride¹⁴⁷.

Treating 3-($\text{RC}_6\text{H}_4\text{OSiMe}_3$, $\text{R}=\text{H}, \text{Me}$) with TeCl_4 in PhMe gave 82-89% below Fig.24 compounds. Bromosalicyldehyde derivative Fig.24 (b) gavetrichlorotellurium derivative Fig.24(c), which is stabilized by carbonyl O-Te interaction¹⁴⁸.

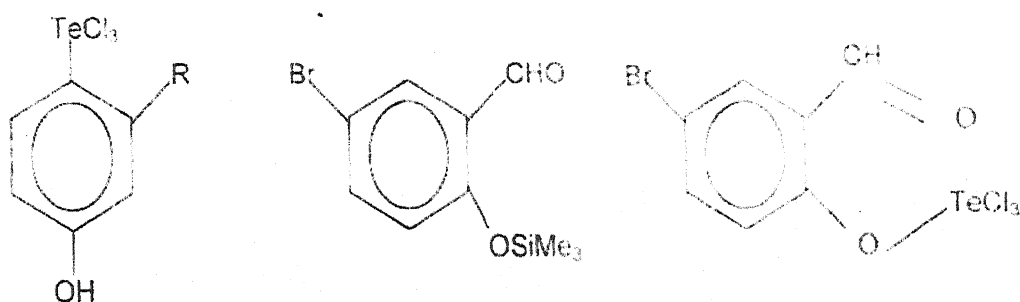


Fig. 24
(43)

$(R_4N)_2 [Ph_2Te(NO_3)_2X_2]^{2-}$ ($R = Me, Et, Bu; X = Cl, Br, I, NO_3$) were prepared and characterized, physicochemical studies suggested are octahedral geometry for the anions¹⁴⁹.

The pentacoordinated Te(IV) complexes $[R_2TeCl_2.L]$ ($R = C_6H_5, p-CH_3OC_6H_4$; $L = Ph_3PSe; (p-MeC_6H_4)_2PSe, (Ph_2P-(Se)(CH_2)_2SePh_2)$) were prepared by the reaction of R_2TeCl_2 with L under anhydrous condition. The reaction of $RTeCl_3$ and L , however yields tellurium/selenium metal $^1J(31P-^{77}Se)$ coupling constant data suggest complexation. In case of bidentate donor bases only one donor site is used in coordination. The complexes possess distorted octahedral geometry around a central Te atom which is surrounded by five groups and one vacant site occupied by a lone pair¹⁵⁰.

Thermal analysis indicated that $4-RC_6H_4TePhX_2$ ($R = H, Me, X = Cl$) form 1:1 complexes with $SbCl_5$. In 1:3 complexes two of the $SbCl_5$ molecules occupy equivalent positions ($R = H, X = I$) forms only 1:3 complex with $SbCl_5$ ¹⁵¹.

$Me_3SiO(Ph = CH_2)$ reacted with $TeCl_4$ in Et_2O and with $RTeCl_3$ ($R = 4-MeOC_6H_4, 3,4-(MeO)_2C_6H_3, (4-EtOC_6H_4)$) in C_6H_4 to give 63% $(PhCOCH_2)_2TeCl_2$ and 87-91% $PhCOPh_2TeCl_2$ respectively¹⁵².

$(p\text{-RC}_6\text{H}_4)_2\text{TeCl}_2$ ($R = \text{H, Br, Me, MeO}$) were prepared in 86-87% yields by refluxing $(p\text{-RC}_6\text{H}_4)_2\text{Hg}$ with TeCl_4 in dioxane one hour, $p\text{-MeOC}_6\text{H}_4\text{TeCl}_2\text{C}_6\text{H}_4\text{R-}p$ ($R = \text{H, Me}$) were prepared in 93-97% yields respectively refluxing $p\text{-MeOC}_6\text{H}_4\text{TeCl}_3$ with $(p\text{-RC}_6\text{H}_4)_2\text{Hg}$ dioxane 8 hours¹⁵³.

The reaction of $(\text{CF}_3)_2\text{TeF}_2$ with BF_3 , AsF_5 and SbF_5 yield the new complex compounds $[(\text{CF}_3)_2\text{Te}][\text{B}_4\text{F}_4]$ and $[(\text{CF}_3)_2\text{TeE}][\text{CF}_6]$ ($E = \text{Sb, As}$) whereas the reaction of $(\text{CF}_3)_2\text{TeX}_2$ ($X = \text{Cl, Br}$) with halide acceptors caused only decomposition $(\text{CF}_3)_2\text{TeX}_2$ form with MX ($X = \text{F, Cl; M} = \text{K, Cs, Ag}$) isolable salts $\text{M}[(\text{CF}_3)_2\text{TeX}_3]$, $\text{M}[(\text{CF}_3)_2\text{TeBr}_3]$ is only detected in solution evidence for the formation of hexa coordinated tellurates(IV) $\text{M}_2[(\text{CF}_3)_2\text{TeX}_4]$ is found¹⁵⁴.

The interaction of organotellurium trichlorides, $p\text{-RC}_6\text{H}_4\text{TeCl}_3$ ($R = \text{H, OH, OCH}_3, \text{OC}_2\text{H}_5$) with Lewis bases (quinoline, 1-methyl-2-pyrrolidinone, tetramethylene sulfoxide or 2-aminothiozole) led to the isolation of 16 Lithertato unknown stable molecular adducts. They were screened for their gridae properties and found to be more active against bacteria than fungi¹⁵⁵.

Diphenacyltelluriumdihalides, dipseudohalide, dioximes, dithiacarbamate derivatives e.g. $\text{PhCOCH}_2\text{TeR}_2$, CH_2COPh ($R = \text{iodo}$) Br , NCS , CN , S_2CNHPh , piperidinodithiacarbamate and adducts with some nitrogen donors, e.g., $\text{PhCOCH}_2\text{TeR}_2(\text{Br}_2)\text{CH}_2\text{COPh}$ ($R^1_2 = \text{pyrralidine, pyridino, piperidino, morpholine}$) have been synthesized and characterized. The

tetracoordinated organotellurium compounds exhibit keto-enol tautomerism with end form being present to the extent of ~50% while the hexacoordinated Te adducts exist in the keto form. The proton of the enol form and hydroxy proton of oximes derivative are attached to the lone pairs of Te atoms forming Te-H bonds¹⁵⁶.

$[\text{HO}(\text{CH}_2)_2]_2\text{NCS}_2\text{H}(\text{LH})$ prepared in solution by mixing $[\text{HO}(\text{CH}_2)_2]\text{NH}$ with CS_2 reacted with Se and Te compounds to give TeL_4 , TeI_2L_2 , TeIL_3 , TeL_2 and SeL_2 . The complexes were characterized by analytical, IR and electronic spectra and thermogravimetric analysis¹⁵⁷.

A freshly prepared solution of tellurocyclopentane diperchlorate reacts with Lewis bases to yield cation complexes $[\text{RTeL}_2](\text{ClO}_4)_2$ (R = cyclopentyl, L = pyridine-N-oxide lutidine, N-Oxide, β -picoline-N-oxide, quinoline-N-oxide, 2,2-bipyridyl). All were characterized and proposed to have a trigonal bipyramidal structure with one lone pair of electrons occupying on the positions¹⁵⁸.

R_2TeL_2 (R = Ph or p - MeOC_6H_4) have been prepared by the reaction of R_2TeCl_2 with NH_4L in anhydrous toluene. The product have been characterized using analysis and spectroscopic IR, ^1H , ^{13}C , ^{125}Te NMR data. The products are monomeric in nature and their possible structures are reported¹⁵⁹.

Several new dimethyl tellurium dicarboxylates $\text{Me}_2\text{Te}(\text{OCOR})_2$ (R = alkyl,

aryl) were prepared in high yield and characterized. A probable nonionic trigonal bipyramidal structure was deduced from spectroscopic and conductance data¹⁶⁰.

Organotellurium compounds $(\text{Ph}_2\text{CH}_2\text{CH}_2)_2\text{TeRX}$ ($\text{R} = \text{Br}, \text{Cl}, \text{cyano}, \text{iodo}, \text{Me}, \text{Et}, \text{CH}_2\text{CHCH}_2\text{Ph}$; $\text{X} = \text{Br}, \text{Cl}, \text{I}$) were prepared and characterised $(\text{PhCH}_2\text{CH}_2)_2\text{TeRX}$ ($\text{R} = \text{alkyl}, \text{same X}$). Readily eliminated Te alkyl halide in DMSO conductivity measurements indicated that the tellurides behave as weak electrolyte¹⁶¹.

Diaryltellurium bis(trihaloacetate) and diarylchlorotellurium trihaloacetates e.g., $(\text{MeOC}_6\text{H}_4)_2\text{Te}(\text{O}_2\text{CCF}_3)_2$ and $(\text{MeOC}_6\text{H}_4)_2\text{TeCl}(\text{O}_2\text{CCF}_3)$ have been prepared by metathetical reaction between corresponding dichloride and AgOCOCF_3 or NaOCOCl_3 respectively. A convenient synthesis of diaryltellurium bis(trifluoroacetate) from the corresponding telluroxides and trifluoroacetic anhydride is reported. These compounds have been characterised by IR, ^1H and ^{19}F NMR spectra and X-ray diffraction studies¹⁶².

12-tetracoordinated diorganotellurium(IV) oximates of the type $\text{Ar}_2\text{TeCl}(\text{ONCRR}')$, $\text{Ar}_2\text{Te}(\text{ONCRR}')_2$ [$\text{Ar} = \text{Ph}, p\text{-MeC}_6\text{H}_4$, $\text{RR}' = \text{Me}, \text{Me:Me}, \text{Ph:Me}, \text{Et:Ph}, \text{Ph:}(\text{CH}_2)_5$] have been synthesized either by the reactions of diorganotellurium (IV) dichlorides with appropriate oxime in the presence of Et_3N or by the metathetical reactions of Ar_2TeCl_2 with the corresponding sodium salt of the ligand. The organotellurium(IV) oximate derivatives have

been characterised by elemental analysis, IR, NMR, molecular weight and conductance data¹⁶³.

Organotellurium oximates R_2TeL_2 ($R_2 = Me_2(p-MeOC_6H_4)_2$, diphenylene $L=8$ -hydroxyquinolate, 8-hydroxy-2-ethylquinolate) have been prepared in quantitative yields by the interaction of R_2TeX_2 ($X = Cl, Br, I$) with NaL or HL . R_2TeL_2 react with R^1CO_2H ($R^1 = CF_3, CCl_3, CHCl_2, CH_2Cl$) to yield mixed ligand complexes $R_2Te(OCOR^1)L$. The proton magnetic and I.R. spectra suggest that R_2TeL_2 possess two types of oxime groups, one of which is bidentate and the other unidentate. The Te atom thus prefers to remain pentacoordinate in an octahedral geometry, one of the sites being occupied by a lone pair¹⁶⁴.

Hydrolysis of bis(hydroxyaryl)tellurium dihalide appears to in a stepwise manner. In neutral medium $R_2Te(OH)X$ ($X = \text{halide ion}$, $R = 4\text{-hydroxy phenyl}$, 3-methyl, 4-hydroxy phenyl) have been isolated. Further, hydrolysis does not occur appreciably. Alkaline hydrolysis (with $NaOH$) yield $R_2Te(OH)_2$ which on heating at $100^\circ C$ changes to R_2TeO . Isolation of the intermediates in this case is not possible but they are indicated by Ph metric and conductometric titrations. Hydrolysis of these compounds, follows the order $Cl > Br > I$ and $O\text{-cresol} > \text{phenol}$ ¹⁶⁵.

Te reacted with RCl ($R = \text{acetyl}$) to give R_2Te , which react with SO_2Cl_2 or $Pb(OAc)_4$ to form R_2TeCl_2 or $R_2Te(OAc)_2$ or R_2Ph_2TeO with maleic anhydride gave $[R'_2Te(\text{maleate})_2]$ ($R^1 = \text{acetyl, Ph}$) which were dimeric.

$[R_2^2Te(SCH_2CH_2CO_2)_2]$ ($R^2 = Ph, 4-MeOC_6H_4$) were prepared from R_2TeO and $HSCH_2CH_2COOH$. R_2^2TeO ($R^2 = 4EtOC_6H_4$) reacted with $HSCH_2COO(CH_2OC_6H_3(6H)Bu-3,4-(HSR^3))$ to give monomeric $R^2Te(SR^3)_2$.

Telluracyclopentane ($R^4 = iodo$) or Ph_2TeCl_2 and $AgO_2CKH:CHCOOBu$ gave monomeric $[R^4 = (OOCCH:CHCOO)-Bu]$ or $Ph_2Te(O_2CCH:CHCO_2Bu)_2$ respectively. Attempt to preparation of hexyl or octyl Te compounds from Te and R^5Br ($R^5 = hexyl, acetyl$) in presence of $Et_4N^+Br^-$ gave $Et_4N^+Te^-Br_3$ which was brominated to form $Et_4N^+Te^-Br_5$ ¹⁶⁶.

Reaction of $(p-RC_6H_4)_2Te(O_2CR^1)_2$ with R^1COCl (1:2) in $CHCl_3$ or CCl_4 gave $(p-RC_6H_4)_2TeCl_2$ and $(R^1CO)_2O$ ($R = H, MeO, R^1 = Me, Ph, Et$)¹⁶⁷.

The reaction of $(p-RC_6H_4)_2TeO$ with $(R^1CO)_2O$ gave sixteen $(p-C_6H_4)_2Te(O_2CR^1)_2$ ($R = H, Me, OMe, NMe_2; R^1 = Me, Ph, ClCH_2, F_3C$). Similarly, $(p-RC_6H_4)_2TeO$ and $RCOOH$ gave $(p-MeO-RC_6H_4)_2Te(O_2CR)_2$ ($R = Me, CCl_3$). The reaction of $(p-C_6H_4)_2TeO$ with HX gave $[(p-RC_6H_4)_2Te^+OX]X^-$ ($R = H, OMe; X = ClO_4, O_2CCCl_3$). Also $(p-RC_6H_4)_2Te(O_2CR^1)_2$ and R^1COCl gave $(p-C_6H_4)_2TeCl_2Me, MeO$)¹⁶⁸.

The compounds $(4-RC_6H_4)_2Te(O_2CR^1)_2$ ($R = H, MeO, R^1 = CF_3, CCl_3, CHCl_2, CH_2Cl$) and $Me_2Te(O_2CCF_3)_2$ were prepared and characterised. Thus Ph_2TeCl_2 was treated with CF_3COOH and Ag_2O in CH_2Cl_2 to give >70% ($R = H, R^1 = CF_3$). The IR spectral data of the compounds indicates that both

haloacetate groups are equivalent. In refluxing PhMe the trichloroacetates undergo decarboxylation followed by elimination of dichlorocarbene and yielding diorganotellurium dichlorides¹⁶⁹.

TeL_2X_2 (L = thiooxime, X = I, Br) and TeL_3X (X = Cl, Br, I) were prepared from Te(IV) solution contained ML and KX. The complexes were characterized by I.R.¹⁷⁰.

$(p\text{-RC}_6\text{H}_4)_2\text{TeO}$ (R = H, Me, MeO, Me₂N) reacted with HCOOH in Me₂CHOH at 60°C to give 61-90% $(p\text{-RC}_6\text{H}_4)_2\text{Te}(\text{O}_2\text{CH})_2$ (same R) which decomposed in refluxing o-xylene to give quant yields of $(p\text{-RC}_6\text{H}_4)_2$ (same R) and HCOOH¹⁷¹.

$\text{RR}'\text{Te}(\text{O}_2\text{CR})_2$ (R = *p*-MeOC₆H₄, *p*-EtOC₆H₄, R' = PhCH₂COPh, CH₂COMeC₆H₄NMe₂-*p*, R² = Me, CH₂, Cl, Ph) prepared by the metathetical reaction of Ag carboxylates and organotellurium dichlorides act as a unidentate ligands. The thermogravimetric curves for [*p*-MeOC₆H₄Te(C₆H₄NMe₂)-*p*](CO₂CR²)₂ (R² = Me, Ph) indicates decomposition at 240°-260°C with loss of 2 moles of CO₂ giving unstable telluraorganotellurium which further decomposed at 380°-400°C yielding R₂²Te. All these compound prepared were anti-bacterial¹⁷².

The compounds R₂TeXY [R = hydroxyaryl, HOC₆H₄, 1,2-(HO)₂-C₆H₃, 1,3-(HO)₂C₆H₃, X, Y = halo, OH] particularly diaryl tellurium hydroxides are prepared in one step process with high yield ~95%, by reaction of R₂TeAB (A, B = halo, OH) with an alkali metal hydroxides. R₂TeXY are useful in precursor of semiconductors. A mixture of (4-HOC₆H₄)₂TeCl₂ and aqueous NaOH was heated at 400°C for 10 min., to give R₂TeXY (R = 4-HOC₆H₄; X=Y=OH)¹⁷³.

Solutions of diorganotellurium (IV) diperchlorates $R_2Te (ClO_4)_2$ ($R = Ph, p-MeOC_6H_4$); may be prepared by the reaction of R_2TeCl_2 and $AgClO_4$ or by the reaction of diorganotelluroxide with excess of 70% $HClO_4$. I.R. and conductivity data indicates that $Ph_2Te (ClO_4)_2$ possesses a covalently bonded perchlorates groups in solution. Interaction of the freshly prepared solutions with Lewis bases affords cationic complexes of the types $[R_2Te(ClO_4)(L)][ClO_4]$ and $[R_2Te(L)_2][ClO_4]_2$ which have been characterized by I.R., elemental analyses and conductivity measurements. The DMSO complex is as (Fig.25).

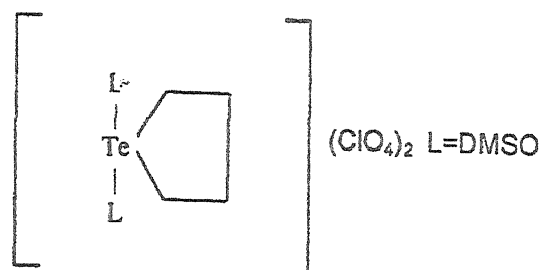


Fig. 25

Explodes at its melting points 174.

$Ph_3TeXTiX_4$ and $2Ph_3TeX.TiX_4$ ($X = Cl, Br$) are obtained by reactions of Ph_3TeCl and Ph_3TeBr with TiX_4 . Ph_3TeI and TiI_4 yield only Ph_3TeI, TiI_4 . Conductivity and molecular weight determination are consistent with their dissociation in dilute solution as Ph_3Te^+ and TiX_5^- or $PhTe^+$ and TiX_6^{2-} units. Far IR spectra reflect the formation of TiX_5^- and TiX_6^{2-} for 1:1 and 2:1 adducts respectively. The formulation of these compounds are given as $[Ph_3Te]^+[TiX_5]^-$

and $[\text{Ph}_3\text{Te}]_2^+ [\text{TiX}_6]^{2-}$.¹⁷⁵

$\text{Ph}_3\text{TeX} \cdot \text{SnCl}_4$ and $2\text{Ph}_3\text{TeX} \cdot \text{SnCl}_4$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) are obtained by reactions for Ph_3TeX with SnCl_4 . Conductance, molecular weight determination and ^1H NMR data are consistent with dissociation of adducts in dilute solution Ph_3Te^+ and SnCl_4X^- or Ph_3Te^+ and $\text{SnCl}_4\text{X}_2^{2-}$ units. The absence of Te-Sn and Te-X vibration in the far IR of these compounds reflect the transfer of X from Ph_3TeX to SnCl_4 . The formulation of these adducts are proposed as $[\text{Ph}_3\text{Te}][\text{SnCl}_5]$, $[\text{Ph}_3\text{Te}]_2[\text{SnCl}_6]$, $[\text{Ph}_3\text{Te}][\text{SnCl}_4\text{Br}]$, $[\text{Ph}_3\text{Te}]_2[\text{SnCl}_4\text{Br}_2]$, $[\text{Ph}_3\text{Te}][\text{SnCl}_4]$ and $[\text{Ph}_3\text{Te}][\text{SnCl}_4\text{I}_2]$.¹⁷⁶

The first synthesis of tetratelluradicyclopentanampntalen which is six membered ring isomer of hexamethylene tetratellurafulvalene from 1,2-dibromocyclopentene and $\text{Cl}_2\text{C}=\text{CCl}_2$ is reported. It was obtained as yellow microcrystals¹⁷⁷.

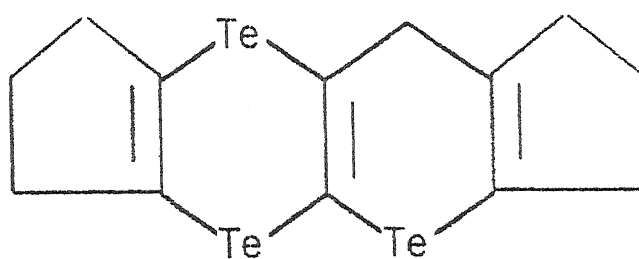


Fig. 26

Diaryl tellurides $\text{RTeR}'\text{R} = \text{R}' = \text{Ph}$, $p\text{-MeOC}_6\text{H}_4$; $\text{R}=\text{Ph}$, $\text{R}' = p\text{-MeOC}_6\text{H}_4$) react with allyl bromide cyclohexyl iodide. MeIPhX ($\text{X} = \text{Br}, \text{I}$) or SnI_4 to give corresponding triorganotellurium halides. the Te-allyl bond is readily cleaved by electrophiles such as Br_2 , I_2 , ICl , BrCN , ICN . Thus $\text{Ph}_2\text{Te}(\text{CH}_2\text{CH}:\text{CH}_2)\text{Br}$, which with I_2 , IBr and BrCN gave 62-85% Ph_2TeIBr , Ph_2TeBr_2 and Ph_2TeBrCN respectively¹⁷⁸.

Reaction of TeCl_4 with $o\text{-or-}m\text{-ClC}_6\text{H}_4\text{OH}$ gave $3,4\text{-Cl(OH)C}_6\text{H}_3\text{TeCl}_3$ and $2,4\text{-Cl(OH)C}_6\text{H}_3\text{TeCl}_3$ respectively which on halogen exchange with KBr and KI gave the corresponding TeBr_3 and TeI_3 . Conductance and cryoscopic measurements show that the TeCl_3 are almost nonionic, whereas the TeBr_3 and TeI_3 re 1:1 electrolytes in PhNO_2 , Me_2SO and MeCN . The ^1H NMR spectra indicate that the TeX_3 ($\text{X} = \text{halo}$) groups are para to the OH group. The far I.R. spectra reflect the polymeric nature of these compounds¹⁷⁹.

Cresyltelluriumchloride were prepared treating cresols with TeCl_4 . Other halides were obtained by halogen exchange of the chlorides with KBr or KI . Conductivity and cryoscopic measurements indicates that RTeCl_3 ($\text{R} = \text{cresyl}$) and R_2TeX_2 , ($\text{X} = \text{halogen}$) are molecular compounds. While RTeBr_3 , RTeI_3 and R_3TeI are ionic compounds¹⁸⁰.

$(4\text{-HOC}_6\text{H}_4)_n\text{TeX}_{4-n}$ ($n = 1$ or 2 , $\text{X} = \text{Br}$, Cl or I) and $(1,2$ and $1,3\text{-(OH)}_2\text{C}_6\text{H}_3)_n\text{TeX}_{4-n}$ ($n = 1, 2$ or 3 ; $\text{X} = \text{Cl}$, Br or I) were prepared. The chlorides by direct reaction of the hydroxyl benzene with TeCl_4 in CHCl_3 , the bromides

and iodides by halogen exchange of the chloride. The conductivity and cryoscopic measurement shows that materials of the type RTeBr_3 and RTeI_3 and R_3TeX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) behaves as 1:1 electrolytes in dilute solutions, whereas compounds with comparisons, R_2TeX_2 exhibits molecular properties and to polymerize at higher concentration¹⁸¹.

$[\text{R}_2\text{Te}(\text{O}-\text{O}-\text{C}_6\text{H}_4(\text{R}^1\text{NR}^2\text{N}:\text{CR}^1-\text{C}_6\text{H}_4\text{O}-\text{O}))]$ ($\text{R}^2 = (\text{CH}_2)_4$, $\text{R} = \text{Ph}$, $p\text{-MeOC}_6\text{H}_4$, $p\text{-EtOC}_6\text{H}_4$, $\text{R}^1 = \text{M}$, $\text{R}^2 = \text{C}_2\text{H}_4$, $\text{R} = \text{Ph}$, $\text{R}^1 = \text{CH}_3$, $\text{R}^2 = \text{CH}_2\text{CH}_2$, $\text{R} = \text{Ph}$, $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{O}-\text{C}_6\text{H}_4$ and $[\text{Ph}_2\text{Te}(\text{O}-\text{OC}_6\text{H}_4\text{CH} = \text{NR}^3\text{X})][\text{R}^3 = \text{O}-\text{C}_6\text{H}_4][\text{X} = \text{O}, \text{S}, \text{R}^3 = \text{C}_6\text{H}_4, \text{X} = \text{O}]$ were prepared and characterized by elemental analysis, electrical conductivity, molecular weight, IR and ^1H NMR measurement. The complexes are monomeric and non electrolytes in PhNO_2 ¹⁸².

R_2TeCl_2 ($\text{R} = \text{Me}, \text{Et}$) reacted in HCl SO_3 to give 40-60% $\text{R}_2\text{Te}(\text{SO}_2\text{Cl})_2$. Electrical conductivity showed to be nonionic and IR spectroscopy gave a reduced Cs symmetry for the SO_3Cl which indicates covalent bonding in it¹⁸³.

Several organotellurium derivatives of the general formula $\text{C}_8\text{H}_8\text{TeX}_2$ ($\text{x} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}, \text{OCOCH}_3, \text{OCOCH}_3\text{Cl}, \text{OCOPh}$), $(\text{R}_4\text{N})^+ (\text{C}_8\text{H}_8\text{TeI}_2\text{X}^-)$ ($\text{R} = \text{Me}, \text{Et}, \text{Bu}$; $\text{X} = \text{Cl}, \text{Br}$) and RR^1TeX_2 ($\text{R} = p\text{-MeOC}_6\text{H}_4$, $\text{R} = \text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2$; $\text{X} = \text{Cl}, \text{OCOCH}_3, \text{OCOPh}$ were tested against five bacteria (*Bacillus subtilis*, *staphylococcus aureus*, *Escherichia coli*, *Salmonella typhi*, *Mycobacterium tuberculosis*, and one fungus (*Aspergillus terreus*).

The antifungal activity of the anionic complexes was higher than their antibacterial activity compared to the parent compound $C_8H_8TeI_2$ ¹⁸⁴.

$RC_6H_4TeX_2C_6H_4R^1$ ($R = H, 4-F, 4-MeO$) $R = H, Me, MeO, X = Cl, Br$) were prepared in 60-90% yields by treating $(RC_6H_4)_2Te_2$ with $R^1C_6H_4N_2^-$ in the presence of $CuCl_2$ or $CuBr_2$ ¹⁸⁵.

The reaction of $(C_2F_5)_2Te$ and XeF_2 in SO_2ClF yielded $(C_2F_5)_2TeF_2$ essentially quantitatively and chlorine and $(C_2F_5)_2Te$ gave $(C_2F_5)_2TeCl_2$. Both $(C_2F_5)_2TeF_2$ and $(C_2F_5)_2TeCl_2$ were assigned a trigonal bipyramidal geometry on the basis of their ^{19}F NMR and vibrational spectra with the lone pair and C_2F_5 groups in equatorial and the halogens in the axial positions. $C_2F_5TeF_3$ was prepared essentially quantitatively by the reaction of $C_2F_5Te \cdot TeC_2H_5$ and XeF_2 in liquid SO_2F_2 . Generally inert SO_2ClF was found to react with $C_2F_5TeTeC_2F_5$ to give $C_2F_5TeClXF_{3-x}$ and SO_2 . The structure of $C_2F_5TeF_3$ was determined by X-ray diffraction. Each tellurium atom is surrounded by two terminal fluorine atoms and two bridging fluorine atoms and a C_2F_5 group in an axial position around the apex of a distorted square pyramidal unit. The square pyramidal units are linked by symmetrical bridging atoms into endless chains with bridging angles of 180° and 177° . The geometry of the $(C_2F_5TeF_4)$ group is consistent with the steric activity of the nonbonded electron pair. The ^{19}F NMR and Raman spectra of $C_2F_5TeF_3$ were recorded and the Raman spectrum assigned *trans* $C_2F_5TeClF_5$ was prepared by the reaction of $C_2F_5TeTeC_2F_5$ and an excess of ClF . The *trans* octahedral geometry of $C_2F_5TeClF_4$ was unambiguously assigned from its ^{19}F NMR and vibrational spectra. A mixture of *trans* $(C_2H_5)_2TeF_4$ and *trans*

$C_2F_5TeCl_4$ was obtained from the reaction of $(C_2F_5)_2Te$ and excess of ClF trans geometry of $(C_2F_5)_2TeF_4$ was unambiguously assigned from its ^{19}F NMR spectrum¹⁸⁶.

The sensitivity and reactivity of some new α,α' - bis(2 and 4 substituted benzoyl) $TeCl_2$ ($R = H, NO_2, CH_2Cl_2, CONH$ etc. $R^1 = H, NO_2, OMe$ etc.) Fig.27 are reported. Te-C bond remains stable in many interesting inter conversions of these derivatives 2-substituted derivatives were intramolecular coordinated with the central metal atom¹⁸⁷.

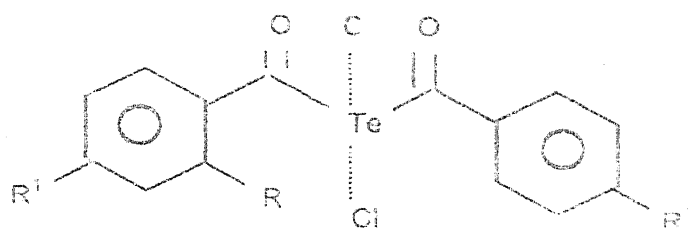


Fig. 27

Electrophilic substitution of Fig.28(a) ($R = H$) with $TeCl_4$, 4hrs refluxing C_6H_6 gave 85% Fig.28(a) ($R = Cl_3Te$) which was heated in an oil bath 1.5hours at 190^0-200^0C to give hydrochloride fig.28(b) The letter was dechlorinated with $Na_2S_2O_7$ followed by neutralization to yield naphthaledene Fig.28(c)¹⁸⁸.

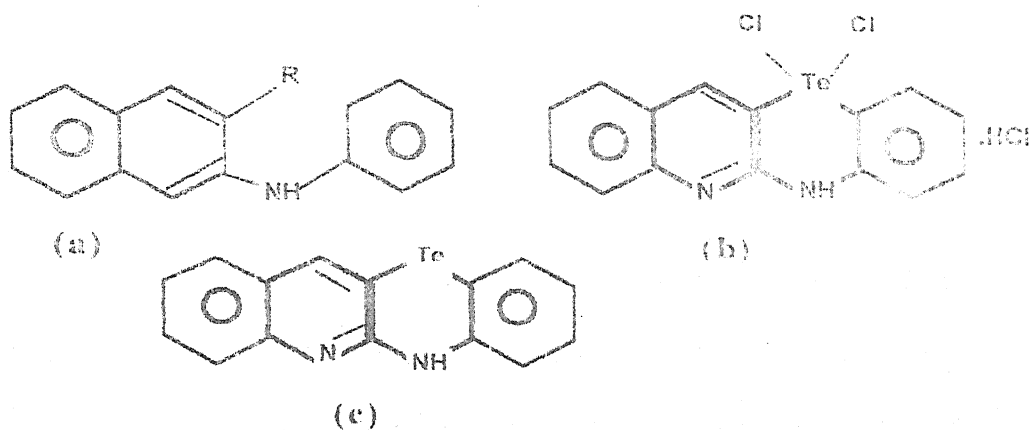


Fig. 28

Trans metalation of RHgCl ($\text{R} = 2\text{-(2-pyridyl)phenyl-2-(quinoline-2-yl)phenyl}$) with TeBr_4 gave organotellurium tribromides RTeBr_3 . Reduction of the tribromides gave RTeBr and dimmers $\text{R(Te)}_n\text{R}$ ($n = 1\text{-}3$)¹⁸⁹.

The reaction of $\text{Bu}_4\text{N[TeF}_5\text{]}$ with $\text{HOCHCH}_2\text{NH}_2$ -1-amino -2 propanol, 2-aminobutanol and 3-amino-1-propanol was followed by ^{19}F and ^{125}Te NMR. The all cases TeO_3L ($\text{L} = \text{Amino alcohol}$) were formed in which there are 3 Te-F hypervalent bonds¹⁹⁰.

The reaction of unsaturated alcohol with aryl tellurium trihalides gave cyclic ethers bearing an aryl dihalotelluro group in β -position.

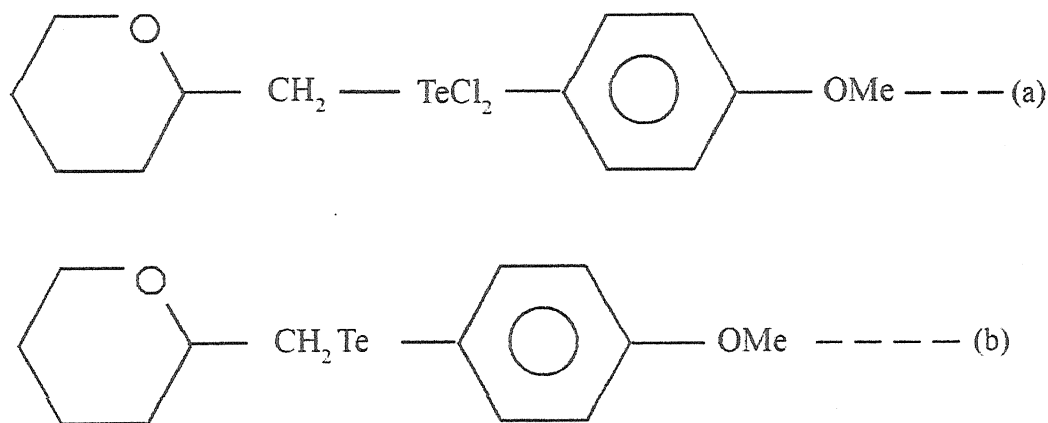


Fig. 29

Reduction of the Te-Cl bond with thiourea dioxide gave the Tellurides. Thus the reaction of $\text{CH}_2\text{-CH(CH}_2\text{)OH}$ with $4\text{-MeOC}_6\text{H}_4\text{TeCl}_3$ gave 90% yield of dihalotelluro ether Fig.29(a) which on reduction gave 93% yield of telluride Fig.29(b)¹⁹¹.

The compounds $R_2Te[(O)N = CMeC(NO)Me]_2$ ($R = ph, anisyl, Me$) were prepared when Ph_2TeO was treated with $MeC(=NOH)C(=NOH)Me$ (when $R = Ph$)¹⁹².

$(PhCOCH_2)_2TeX_2$ ($X = Br, iodo, SCN$) S_2CNR_2 ($NR_2 = anilino, piperidino$) and $(PhCOCH_2)_2TeBr_2(NR^1_3)_2$ ($NR^1_3 = amines$) were prepared. Spectral studies indicated that the tetracoordinated tellurium compounds $(PhCOCH_2)_2TeX_2$ exhibited keto-enol tautomerism (enol form to the extent of 60%). The hexa coordinated Te compounds $(PhCOCH_2)_2TeBr_2(NR^1_3)_2$ ¹⁹³.

The reactions of $\alpha-Me_2TeI_2$ with $M_2(CO)_{10}$ ($M = Mn, Re$) $CO_2(CO)_8$, $Na(Co(CO)_4)$ and $Na(Mn[CO]_5)$ gave $cisM(CO)_4Te(Me_2)I$, $[Co(CO)_5TeMe_2]_2$, $[Co(CO)_4]_2TeMe_2$ and $Mn(CO)_5TeMe_2$ respectively $(Cp Mo(CO)_3)_2$ ($Cp = cyclopentadienyl$) did not react with $\alpha-Me_2TeI_2$ whereas $(MeCp)MN(CO)_3$ ($MeCp = methyl cyclopentadienyl$) gave a brown oil. The complexes were characterized by I.R. spectra¹⁹⁴.

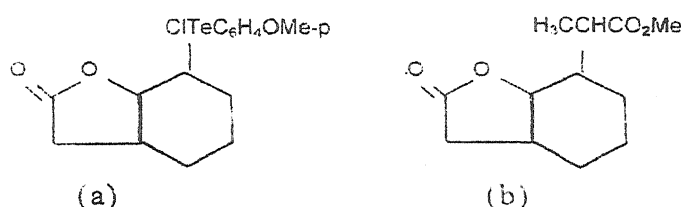


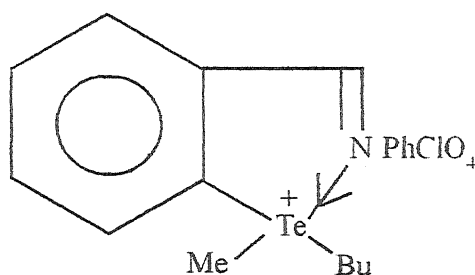
Fig. 30

The lactones fig.30(a) and cyclic ethers produced in the tellurocyclo functionalisations of unsaturated carboxylic acids and alcohol are efficiently detellurated with $CH_2=CHCO_2Me$ leads to the corresponding adducts Fig.30(b) in moderate to good yield¹⁹⁵.

1-(NMe₂)-4-MeC₆H₄ on o-mercuration followed by reaction with ArTeCl₃ (Ar = Ph, 4-MeOC₆H₄ or 4-EtOC₆H₄) gives 1-(NMe₂)-2-(Ar-TeCl₂-4-Me-C₆H₃) which on reduction with Na₂S₂O₅ gives 1-Me-3-N-2-TeAr-4-Me.C₆H₃(L).L were characterized by elemental and typical reaction with MeI, IR, ¹H, ¹³C NMR spectra, molecular weight and conductance measurements. L reacts with Na₂MCl₄/K₂MCl₄ (M = Pt or Pd) resulting the MCl₂.L. These complexes are monomeric nonelectrolytic and diamagnetic indicating square planar arrangements of ligands around the metal which is supported by electronic spectra. ¹H NMR data in conjunction with IR spectra suggest that L behave as bidentate ligands in these complexes¹⁹⁶.

Lithiation of Ph₂CH₂NMe₂ followed by reaction with Te(S) and air oxidation gives a poorly defined tellurium anhydride. Halogenolysis with Br or SO₂Cl₂ gives o-Me₂NCH₂C₆H₄TeX₃ (X = Br, Cl). Lithiation of PhCH₂NMe₂ followed by reaction with Te(S) then an alkyl halide, then SO₂Cl₂ give o-R¹TeCl₂.C₆H₄CH₂NMe₂ (R = Me, Et, Bu). The structure of o-Me₂NCH₂C₆H₄TeX₃ (X = Br) and the HCl salt of o-X₂TeCl₂C₆H₄CH₂NMe₂ (X = Br) were determined by X-ray crystallography. The coordination of Te in both compounds is essentially octahedral with vacant equatorial site₁₉₇.

The butyl methyl [2-[(phenylimino)methyl] phenyl tellurium perchlorate compound was prepared in 78% yield by treating 2-BuTeC₆H₄CH:NPh with MeI in Me₂COCl and then



With $\text{AgClO}_4 \cdot 3\text{MeCHI}$. The structure was determined by X-ray crystallography¹⁹⁸.

Me_2TeX_2 ($\text{X}=\text{Cyano}, \text{NCO}, \text{N}_3$) have been synthesized by metathesis of Me_2Te with two equivalent AgX in CHCl_3 . Reactions of $\text{Me}_2\text{Te}(\text{N}_3)_2$ with Ph_3P and $\text{Me}^+\text{N}^-\text{Cl}$ yields $\text{Me}_2\text{Te}(\text{N}=\text{PPh}_3)_2$ and $\text{Me}_2\text{N}^+\text{Me}_2(\text{N}_3)_2\text{Cl}^-$ respectively¹⁹⁹.

Halogenation of butyl tellurobenzal anilines ($\text{R}=\text{H}, \text{R}^1=\text{H}, \text{Me}, \text{MeO}, \text{R}=\text{R}^1=\text{F}; \text{R}^2=\text{Bu}$) gave halogenotellurobenzalanilines ($\text{R}^2=\text{Cl}, \text{Br}, \text{Iodo}$) and ($\text{R}^2=\text{Cl}, \text{Br}, \text{Iodo}$). The effects of structural feature upon the length of M-Te intramolecular coordination bonds were studied by X-ray and $^{125}\text{TeNMR}$ ²⁰⁰.

Reaction of R_2Te_2 ($\text{R}=\text{Ph}, 4\text{-MeC}_6\text{H}_4$) with Na in THF containing HMPA generated tellurolate anions which on treatment with SO_2Cl_2 gave 80% $\text{R}(\text{Et})\text{TeCl}_2$, which on treatment with $\text{NaOCH}_2\text{CF}_3$ in $\text{CF}_3\text{CH}_2\text{OH}$ gave 77-78% $\text{R}(\text{Et})\text{Te}(\text{COOCF}_3)_2$ ²⁰¹.

Cyclohexene or cycloheptene reacts with TeCl_4 or TeBr_4 and an alcoholic in CCl_4 to give the 2-alkoxy-trans-cycloalkyltellurium (IV) trihalides com-

pounds ^{13}C and ^1H NMR and mass spectral data were reported ²⁰².

Reaction of $p\text{-RC}_6\text{H}_4\text{COCl}_2$ ($\text{R}=\text{MeO}, \text{O}_2\text{N}$) with $\text{Te}(\text{S})$ and NaI gave 52.73% $(p\text{-RC}_6\text{H}_4\text{CO})_2\text{TeI}_2$. Demethylation of $(p\text{-RC}_6\text{H}_4\text{CO})_2\text{TeI}_2$ ($\text{R}=\text{O}_2\text{N}$) gave $(p\text{-RC}_6\text{H}_4\text{CO})_2\text{TeI}_2$ ($\text{R}=\text{OH}$). Underwent acetylation and chloroacetylation without cleavage of the C-Te bond²⁰³.

The reaction of methyl ketones, RCOCH_3 ($\text{R}=\text{Ph}, 4\text{-MeC}_6\text{H}_4, 2\text{-thienyl}, \text{Me}_3\text{C}$) with TeCl_4 in CHCl_3 gives 29.56% $(\text{RCOCH}_2)_2\text{TeCl}_2$ which were reduced to the corresponding diketo tellurides (3-tellurapentane-1,5-diones, $(\text{RCOCH}_2)_2\text{Te}$) by aqueous $\text{Na}_2\text{S}_2\text{O}_4$. Physical and chemical properties of dike to telluride's are also reported²⁰⁴.

Iodine monohalides (ICl, IBr) CNi and $(\text{SCN})_2$ add oxidatively to R_2Te ($\text{R}=\text{Ph}, p\text{-CH}_3\text{OC}_6\text{H}_4$) under mild condition ($\sim 5^\circ\text{C}$). The resulting organotellurium(IV) derivatives e.g. Ph_2TeICl , undergo to yield several new diaryl tellurium(IV) pseudohalide derivatives e.g. Ph_2TeICN and $\text{Ph}_2\text{Te}(\text{CN})_2$ ²⁰⁵.

The synthesis of $[\text{HOS}_3(\text{CO})_{10}](\text{M}-\text{TeC}_6\text{H}_4\text{OMe})$ by the room temperature. Reaction of $[(\text{Ph}_3\text{P})_2\text{N}][\text{HOS}_3(\text{CO})_{11}]$ with $[(\text{COMe})\text{C}_6\text{H}_4]_2\text{TeCl}_2$ and its conversion into $[\text{OS}_3\text{Te}(\text{CO})_9]$ under thermolysis are reported²⁰⁶.

Reactions of diaryl telluroxide R_2TeO ($\text{R} = \text{Ph}, 4\text{-MeOC}_6\text{H}_4$) with $\text{Me}_3\text{S}^+\text{O}^-$ in MeCNH_2O gave 61-72% $(\text{R}_2\text{TeI})_2\text{O}$. Heating R_2TeO ($\text{R}=\text{Ph}, 4\text{-MeO-C}_6\text{H}_4, 4\text{-tolyl}$) with MeI gave 82.99% R_2TeI_2 . Treating R_2TeO ($\text{R}=\text{Ph}, 4\text{-MeO-C}_6\text{H}_4, 4\text{-tolyl}$) with MeI gave 82.99% R_2TeI_2 .

$\text{Me}_2\text{CHC}_6\text{H}_4$) with $(\text{R}'\text{O})_2\text{SO}_2$ ($\text{R}' = \text{Me}, \text{Et}$) gave 91-96% bis (diarylakoxytellurium) sulfates $[\text{R}_2\text{Te}(\text{OR}') \text{O}]\text{SO}_2$ ²⁰⁷.

Reactions of 4- $\text{MeC}_6\text{H}_4\text{COCH}_2\text{Bu}_2$ with Se and Te gave (4- $\text{MeC}_6\text{H}_4\text{COCH}_2$)₂XBr₂ (X=Se,Te). Adducts of (4- $\text{MeC}_6\text{H}_4\text{COCH}_2$)₂XBr₂ were prepared with morpholine, piperidine and Me_2NH . Condensation of (4- $\text{MeC}_6\text{H}_4\text{COCH}_2$)₂XBr with diamines, hydrazines and semicarbazides gave heterocycles and $[\text{RN}=\text{C}(\text{C}_6\text{H}_4\text{Me-4-CH}_2)_2\text{XBr}_2$ ($\text{R} = \text{OH}, \text{NHCSNH}_2, \text{NHCONH}_2, \text{NHphNHC}_6\text{H}_3(\text{NO}_2)_2\text{-2,4}$]. The prepared compounds were tested for bacterial and fungicidal activity²⁰⁸.

R_4Te ($\text{R} = \text{Me}, \text{Bu}, \text{Me}_3\text{SiCH}_2, \text{vinyl}$) were prepared by treating TeCl_4 with equivalent LiR or RMgX and decomposed thermally and photolytically via a free radical pathway while $(\text{CH}_2=\text{CH})_4\text{Te}$ decomposed by moncouple reductive elimination. Treating TeCl_4 with 4 equivalent Me_3CLi and $\text{CH}_2=\text{CH}_2\text{MgCl}$ gave the corresponding R_2Te directly $(\text{Me}_3\text{C})_2\text{Te}$ was also isolated as a minor product from the reaction of Me_3CTeLi with Me_3CLi in THF. $(\text{CH}_2=\text{CHCH}_2)_2\text{Te}$ was prepared from Li_2Te and 2 equivalent $\text{CH}_2=\text{CHCH}_2\text{I}$ in THF. These compounds were characterized by ^1H , ^{13}C and ^{125}Te NMR spectroscopic²⁰⁹.

$\text{TeR}^1(\text{S}_2\text{CNR}_2)_n$ ($\text{R}^1 = 2\text{-PhN:NC}_6\text{H}_4\text{CN}$, $\text{R}_2 = \text{Me}, \text{Et PhCN}_2$ $n=1,3$) were prepared and characterized by ^{125}Te NMR data indicate dissociation of $\text{TeR}^1(\text{S}_2\text{CNR}_2)_n$ ($n=3$) to $\text{TeR}^1(\text{S}_2\text{CNR}_2)_n$ ($n=1$) in solution and ^{125}Te mossbauer data suggest that $\text{TeR}^1(\text{S}_2\text{CNR}_2)_n$ ($n=3$) are better formulated as charge transfer compounds $\text{TeR}^1(\text{S}_2\text{CNR}_2)_2 \text{S}_2(\text{SCNR}_2)_2$. The crystal and mo-

molecular structure of $\text{TeR}^1 (\text{S}_2\text{CNR}_2)_n$ ($\text{R}=\text{Me}$, $n=1$) determined by X-ray diffraction showed a distorted planar environment for Te^{210} .

I.R. indicates that the undentate NO_3 group in $\text{Ph}_2\text{Te}(\text{NO}_3)_2\text{L}$ ($\text{L} = \text{pyridine}$, N-Oxide , Ph_3PO , DMSO , $1\text{-methyl-2-pyrrolidinone}$, $\text{tetramethylpiperidine}$, $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$ on $2,2\text{-bipyridine}$ formed from $\text{Ph}_2\text{Te}(\text{NO}_3)_2$ and L is covalently bonded²¹¹.

Synthesis of bis(alkyltelluro) methanes are reported. ^{125}Te NMR chemical shifts measured in CDCl_3 are reported relative to neat Me_2Te and range from 213.5 ppm for $(\text{MeTe})_2\text{CH}_2$ to 713 ppm for $(\text{Me}_3(\text{Te})_2\text{CH}_2)$. The dihalides of bis(methyltelluro) and bis(phenyl telluro) methane were prepared and yield chemical shifts in the relatively narrow range of 786 ppm for $\text{CH}_2(\text{TeMe})_2$ to 834 ppm for $\text{CH}_2(\text{TeClMe})_2$. The trends in the chemical shifts and the ^{125}Te mossbauer parameters are compared with those previously reported for the diorganyl tellurides and their halides²¹².

^{19}F chemical shifts were obtained for $4\text{-RC}_6\text{H}_4\text{XC}_6\text{H}_4\text{F-4}$ ($\text{R} = \text{Me}_2\text{N}$, MeO , Me , H , F , Cl , Br , $\text{X}=\text{Te}$, TeCl_2) and ^{13}C chemical shifts were obtained²¹³.

ΔThe ^{125}Te NMR shifts for Ph_4Te (508.9 ppm) and bis (2,2'-biphenylene) TeI (486.3) ppm were measured at ambient temperature together with the ^{125}Te mossbauer parameters for the heat solids. Ph_4Te (δ 0.09, Δ 5.60 mmS^{-1}) I (δ 0.42, Δ 6.40 mmS^{-1}) at 4.2K. These results are compared with those for other

organotellurium compounds. The mass spectra of these compounds are also reported)²¹⁴.

¹²⁵Te mossbaur parameters were measured at 4.2⁰ K for *p*-RC₆H₄)₂TeF₂, *p*-RC₆H₄TeF₃, (*p*-RC₆H₄)₂Te(OAC)₂, (*p*-RC₆H₄)₂Te(OBu)₂, (R = H, EtO, MeO, Me), Ph₂MeTeI and PhMe₂TeI. The structure of difluoride was the similar to that of other halides whereas the coordination of trifluorides was different from that of the other trihalides. The dicarboxylates had parameters similar to that of dihalides. Suitable changes in the coordination about Te occurred with changes in the acyl ligand²¹⁵.

The reaction of thirteen aliphatic ketones with TeCl₄ was studied with ¹H, ¹³C and ¹²⁵Te NMR. TeCl₄ adds electrophilically to the α-carbon of the enol to form keto tellurium trichlorides. Unsymmetrical ketones gave mixture of isomeric ketonyl tellurium trichlorides. Steric hindrance determined which Ketonyltellurium trichlorides form. Except for the ketonyl tellurium trichloride form 2-butanone Te reacts preferentially with the least substituted α-C. Six methyl alkyl ketones also yielded appreciable amount of diketonyl tellurium dichlorides. In all diketonyl tellurium dichlorides, Te is bonded to less hindered methylene carbons²¹⁶.

³⁵Cl NQR spectra are reported for RR¹TeCl₂ (R = Ph, R¹ = Cl; R = Ph, R¹ = 3, 4-(MeO)₂C₆H₃, R = R¹ = 3, 4-(MeO)₂C₆H₃) splittings in the NQR spectrum of PhTeCl₃ are consistent with the reported polymeric structure of this compound. With a square pyramidal six coordination polyhedron for Te,

decreasing Te-Cl bond length corresponded to increase in NQR frequency of the participating Cl atom. A correlation between NQR frequency on Te-Cl bond length was valid for organotellurium chloride without bridging Cl atom²¹⁷.

Bis(*P*-phenoxy phenyl) tellurium dichloride is monoclinic space group $P^{21/C}$ with $a = 8.063(27)$, $b = 21.695(5)$, $c = (12.622)2\text{\AA}$ and $\beta = 101.57(2)^\circ$ $Z = 4$. Final $R = 0.055$ for 2135 reflections. At coordination are given, the compounds adopts a primary four coordinate geometry based on distorted trigonal bipyramidal with an equatorial lone pair. A weak Te-Cl secondary interactions links, the molecule into centrosymmetric dimers²¹⁸.

Crystals of bis (4-phenoxy-3-methylphenyl) tellurium(IV) dichloride are monoclinic space group $P^{21/C}$ with $a = 14.651(3)$, $b = 12.787(3)$, $c = 8.279(2)\text{\AA}$ and $\beta = 92.64(2)^\circ$ $Z = 4$. $R = 0.0298$ for 1907 observed reflections, at parameters are given. The coordination about Te is trigonal bipyramidal with a vacant equatorial position Cl atoms axial and aryl ligands equatorial. An intermolecular OH-Cl hydrogen bond occurs in the crystal. But unlike other $R_2\text{TeCl}_2$ structure, there is no significant secondary bonding between Te and Cl in neighbouring molecules²¹⁹.

The (*p*-phenoxy phenyl) tellurium trichloride is triclinic space group P^1 with $a = 8.521(2)$, $b = 10.917(2)$, $c = 14.813(2)\text{\AA}$ $\alpha = 81.84(1)$ $\beta = 83.38$, and $\gamma = 88.41(1)^\circ$, $Z = 2$. The final $R = 0.0359$ ²²⁰.

The (*p* - bromophenyl) dichloro (Phenyl) tellurium (IV) is triclinic space

group P_1 with $a = 11.257(7)$, $b = 10.817(4)$, $c = 12.358(5)$ Å $\alpha = 82.61(4)$ $\beta = 80.72(5)$ and $\gamma = 69.38(4)^\circ$ $Z = 2$ (2 mole) for $d_c = 2.067$ and $d_o = 2.06$ final $R = 0.048$, $R_w = 0.052$ for 3428 reflections. The structure consist of discrete tetramers in which individual molecules are linked through weak Te-Cl interactions²²¹.

The dichloro bis (*p*-methoxyphenyl) tellurium (IV) i.e., $\text{TeCl}_2 (\text{C}_7\text{H}_7\text{O})_2$ is triclinic space group P_1 with $a = 10.245(5)$, $b = 12.480(94)$, $c = 13.654(4)$ Å $\alpha = 109.22(2)$ $\beta = 80.42(3)$ and $\gamma = 77.30(3)^\circ$ $d_o = 1.75$ and $d_c = 1.76$ for $Z = 4$ final $R = 0.028$ for 3406 unique observed reflections. At coordinates are given. The structure consists of isolated step like tetramers in which two independent molecules and their centrosymmetric equivalents are linked through Te - Cl secondary interactions the Te-Cl bonds occupy the equatorial and axial positions, respectively in the saw-horse structure. The Ph rings are in a propeller arrangement²²².

The tetrakis(L-hydroxy ethyl) dithiacarbamate tellurium(IV) i.e., $\text{C}_{20}\text{H}_{40}\text{N}_4\text{O}_8\text{S}_8\text{Te}$ is triclinic space group PI with $a = 9.008(2)$, $b = 17.194(4)$, $c = 14.501(2)$ Å $\alpha = 127.38(2)$, $\beta = 9.60(2)$ $\gamma = 97.13(2)^\circ$ $Z = 4$ for $d_c = 1.654$, $R = 0.042$ and $R_w = 0.045$ for 3482 reflections. The central Te is bonded to all eight atoms in a highly distorted dodecahedral configuration. The two planar trapezoids, each contain a Te-S bond lengths are $2.637(4) - 2.857(4)$ Å the average being $2.738(4)$ Å. The extensive H-bonding of the terminal OH groups $2.678(13) - 2.676(14)$ Å hinderd the autoredox reaction in TeL_4 and also pro-

vides stability for the crystal packing²²³.

$(\text{C}_6\text{H}_5)_2\text{TeF}_2$ is monoclinic space group C_6 with $a = 11.088(6)$, $b = 20.040(1)$, $c = 13.208(5)\text{\AA}$ and $\beta = 109.07(4)^\circ$ $Z = 4$ (2 moles/ Z) pairs of crystallography independent molecules are linked by two weak secondary Te-F intermolecular bond. The structural model was refined by full matrix least squares to $R = 0.035$ for 162 reflection. Atomic coordinates are given. The stereochemistry of primary bonding about Te is trigonal bipyramidal as for other R_2TeX_2 species and is compared with that of $(\text{Ph}_2)\text{TeF}_2$. The difference in the stereochemistry of the primary bonding about Te can be attributed to the influence of the more electron withdrawing C_6H_5 group, and relates to different secondary bonding and the crystal packing ^{125}Te NMR coupling constants are reported for this and two related compounds previous ^{125}Te Mossbauer data are discussed with regard to the structure²²⁴.

The bis(2-hydroxy ethyl) dithiocarbamate diiodo tellurium(IV) i.e., $\text{Te}(\text{C}_5\text{H}_{10}\text{NO}_2\text{S}_2)_2\text{I}_2$ is triclinic space group $P1$ with $a = 10.740(7)$, $b = 11.536(6)$, $c = 11.000(8)\text{\AA}$ $\alpha = 108.90(5)$ $\beta = 121.94(5)$ and $\gamma = 90.86(5)^\circ$ $dm = 2.29$ and $dc = 2.316$ for $Z = 2$, $R = 0.062$. The atomic parameters are given. The Te atom is seven coordinated to 4 S atoms to two axial I atoms and to an intermolecular bridging I in a distorted pentagonal bipyramidal geometry. The 2S atoms in each bidentate ligands forms unequal bonds. The dithiocarbamate parts of the two ligands are planar²²⁵.

Crystals of $\text{Ph}_2\text{Te}(\text{S}_2\text{CNet}_2)_2$ are monoclinic; one modification has space group pz_1 . A 2nd modification has space group C2/C . Crystals of $\text{Ph}_2\text{Te}[\text{S}_2(\text{OEt})_2]$ are orthorhombic. All three structure are monomeric and contain a stereochemistry active lone pair at the Te atom making it effectively, seven coordinated in each cases²²⁶.

Crystal structure analysis shows that $(\text{Ph}_2\text{TeNCS})_2\text{O}$ is molecular in the solid states. The molecule has two fold symmetrical, with rotation axis passing through O atom and bisecting the Te-O-Te angle. The ether like Te-O-Te moiety is bent $121.4(4)^\circ$ with Te-O distance of $1.985(4) \text{ \AA}$. An intermolecular Te-S contact at $3.416(3) \text{ \AA}$ completes a square pyramidal geometry around the Te atom and links the molecules into chains running parallel to the C-axis. The Te-N bond distance $2.40(1) \text{ \AA}$, indicates a tendency towards ionic character in the bond²²⁷.

X-ray crystal structure of $[(\text{C}_6\text{H}_5\text{TeCl}_2)_2]_2\text{CH}_2$ and $(\text{TeCl}_3)_2\text{CH}_2$ were also determined²²⁸.

The crystal structure determination of $\text{Ph}_3\text{Te}(\text{S}_2\text{CN})(\text{CHMe}_2)_2$ indicates a most unusual dimeric structure in which the ligand can be considered as acting as bridge with very long Te-S bonds. The immediate environment about each tellurium atom can be described as that of a distorted octahedron. The three Te-C(phenyl) bonds are mutually cis with two long Te-S bonds of similar length and a lone pair completing the octahedron²²⁹.

Reactions of Te(IV) with excess phenylene thiourea(L) in aqueous methanolic HCl gave $[\text{TeL}_4]\text{Cl}_2 \cdot 2\text{HCl}$. The crystals are monoclinic space group $p 2_1/c$ $a = 13.939(5)$, $b = 6.520(9)$, $c = 4.873(2)\text{\AA}$ and $\beta = 100.29(4)^\circ$ d (calculated) = 1.651 g cm^{-3} $Z = 2$ Final $R = 0.055$ and $R_w = 0.056$ for 918 independent reflections. The Te atom is bonded to 4 phenylene thiourea S atoms in a square planar arrangement with $\text{Te-S}(1) = 2.678(6)$ $\text{Te-S}(2) = 2.674(5)\text{\AA}$ and $\text{S}(1) \text{Te-S}(2) = 90.5(3)^\circ$. The ligand behaves as a thione or atoms remains outside the coordination sphere of the Te and stabilize the packing arrangement in the unit cell through H-bondings to N atoms²³⁰.

The reactions of Ph_2TeCl_2 with Schiff bases $\text{O-HOC}_6\text{H}_4(\text{R}) = \text{NNH}_2$ ($\text{R} = \text{H, OH}$) and hydrazine derivative Fig. 31 ($\text{R}^1 = \text{H, Cl, Br}$, $\text{R}^2 = \text{H, Me}$) gave Ph_2TeL_2 and $4\text{Ph}_2\text{TeL}^1$ respectively. The compounds exhibited a pseudooctahedral structure in which the Te atom was in a sp^3d^3 hybridized state resulting in pentagonal bipyramidal geometry with stereochemistry, inert lone pair of electron occupying an equatorial position²³¹.

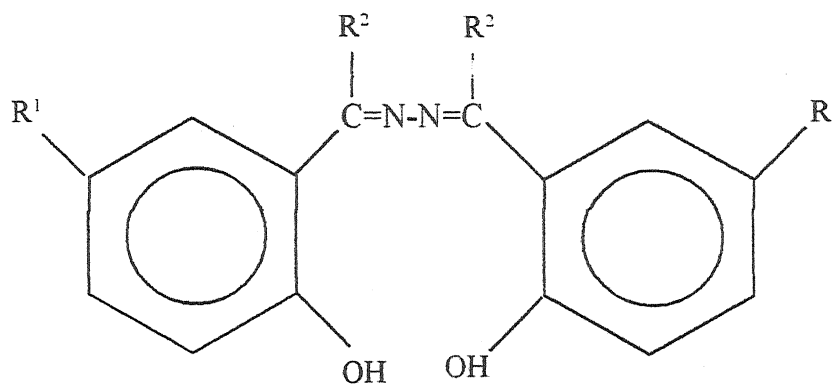


Fig. 31

Some diorganotellurium(IV) complexes $(4\text{-RC}_6\text{H}_4)_2\text{TeL}$ [$\text{R} = \text{H}, \text{OMe}, \text{Oet}$], a tetradentate and tridentate Schiff bases derived from $(\text{MeCO})_2\text{CH}_2$ and $\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2$ or $2\text{-H}_2\text{NC}_6\text{H}_4\text{XH}$, ($n = 2, 3$ $\text{X} = \text{O}, \text{S}$) were prepared and characterized by elemental analysis, conductance, molecular weight, I.R. and ^1H NMR data²³².

$\text{RR}^1\text{TeSalen}$ ($\text{R} = p\text{-R}^2\text{OC}_6\text{H}_4$) ($\text{R}^2 = \text{Me}, \text{Et}$); $\text{R}^1 = p\text{-C}_6\text{H}_4\text{NMe}_2$, CH_2COCH_3 or CH_2Bu), and salen is the dianion of N, N' -ethylene bis(salicylideneimine) were synthesized. I.R. and PMR spectral data established metal ligand bonding and the resulting geometry of the complex²³³.

α -lithio derivatives of furanthiophene benzo(6) thiophene, pyridine and *M*-tosyl pyrrol and diiodole as well as 4-lithio dibenzo thiophene react readily with Te in THF representative conversions of the resulting heterocyclic Li tellurolates to ditellurides alkyl tellurides and telluroacetate are reported²³⁴.

Several sulfonamide Schiff base complexes of the Te(IV) were prepared and characterized using conductivity measurements and I.R. and NMR spectra, elemental analysis confirmed a 1:2 (Metal-Sulfonamide Schiff base) stoichiometry most of the complexes proved to be biologically active (antibacterial hypoglycemic antiinflammatory) as evidenced by pharmacological tests²³⁵.

Treating iminophenols (Fig.32) ($\text{R} = \text{R-OMe}, 3\text{-F}, 4\text{-Br}; \text{R}^1 = \text{H}, \text{O}_2\text{N}$) with $\text{Me}_2\text{Te}(\text{OMe})_2$ gave 80-93% Fig.33 compounds (same R, R^1)²³⁶.

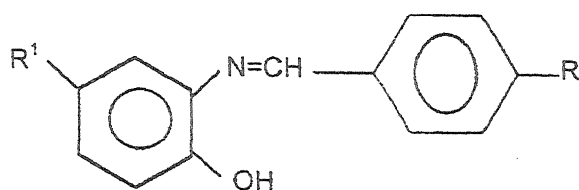


Fig. 32

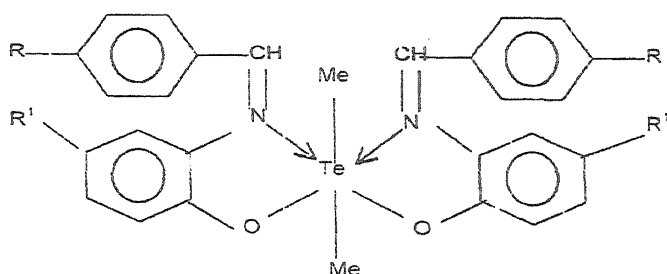


Fig. 33

Square pyramidal complexes $\text{PhTeCl}_3\text{R}^1\text{CR}^2\text{:NNHCSNH}_2$ ($\text{R}^1 = \text{Ph}$, 2- HOC_6H_4 , $\text{R}^2 = \text{H}$, Me) were prepared. Other synthesized compounds were $\text{Ph}_2\text{TeCl}_2\text{R}^1\text{CR}^2\text{:NNHCSNH}_2$ and $(4\text{-R}^3\text{C}_6\text{H}_4)_2\text{Ph.CH:NNHCSNH}_2$ ($\text{R}_3 = \text{Me}$, OMe)²³⁷.

A wide series of diorganyl diaryloxytelluranes e.g., ($\text{R} = \text{Me}$, $\text{R}^1 = \text{H}$, 4- NO_2 , 5- NO_2 , $\text{R}^2 = 4\text{-NO}_2$, 3- NO_2 , 4-Br, H, 4-Me, 4-MeO, 4-NMe², $\text{R} = \text{CH}_2\text{Ph}$, 4-MeC₆H₄, $\text{R}^1 = \text{H}$, $\text{R}^2 = 4\text{-MeO}$) having an azomethine function in the position ortho to the Te atom have been synthesized by the reaction of diorganyl dimethoxytelluranes with benzylidene o-aminophenols. The X-ray structure of dimethyl-bis [2-(4-nitrobenzalideneimino)phenoxy] tellurane ($\text{R} = \text{Me}$, $\text{R}^1 = \text{H}$, $\text{R}^2 = 4\text{-NO}_2$) indicates the presence of an intramolecular Te-N coordination

bond.

According to the dipole moment data and the ^1H , ^{125}Te and ^{14}N NMR spectra compounds (excluding those with $\text{R}^2 = 4\text{-NO}_2$) retain the Te-N coordination in nonpolar solvents²³⁸.

The reactions of thiosemicarbazones and semicarbazones of benzaldehyde, salicylaldehyde, acetophenone and 2-hydroxy acetophenone with TeCl_4 give $\text{Te}(\text{HL})\text{Cl}_4$, TeCl_3 and Te_2LCl_7 (HL = semicarbazone or thiosemicarbazone). The structural features of these Te derivatives are explored by I.R. ^1H , ^{13}C and conductance (in MeCN) measurements and structure based on octahedral arrangement of ligand around Te are proposed. The presence of facial and meridional isomer in equilibrium is indicated in some cases. The complexation occurs through S/O. The nitrogen of the CN group of O^- (if present on benzene ring) TeL_2Cl_7 seen to have Cl bridged and octahedrally coordinated Te²³⁹.

(IV) Compounds in Oxidation State(IV)

This oxidation state of tellurium is not very common. Till 1974, only $(\text{C}_2\text{F}_5)\text{TeF}_4\text{Cl}$ and $(\text{C}_2\text{F}_5)_2\text{TeF}_4$ were reported by Desjardins²⁴⁰. Later on, CH_3TeF_5 was prepared²⁴¹. The presence of some tellurium fluoroanions TeF_7^{2-} ²⁴², TeF_8^{2-} ²⁴² and $\text{TeO}_2\text{F}_4^{2-}$ ²⁴³ has also been established by IR and Raman spectra.

The reactions of phenyl tellurium(VI) fluorides PhTeF_5 , $\text{trans-}[\text{Ph}_2\text{TeF}_4]$ and $\text{mer-}[\text{Ph}_3\text{TeF}_3]$ with alcohol and amines or their trimethyl silyl derivatives are known. The products $[\text{PhTeF}_4\text{X}]$, $[\text{Ph}_2\text{TeF}_3\text{X}]$ and $[\text{Ph}_3\text{TeF}_2]$ ($\text{X} = \text{OMe}$,

NMe₂, NEt₂) were characterized by ¹⁹F NMR spectroscopy and disomeric structures are assigned on the basis of their NMR spectroscopy samples of trans-[Ph₂TeF₄] contain small amounts of cis-[Ph₂TeF₄]²⁴⁴.

The hydrolysis of PhTeF₅, trans-[Ph₂TeF₄] and mer-[Ph₃TeF₃] is known. The hydrolysis products (PhTeF₄OH, Ph₂TeF₃OH and Ph₃TeF₂OH, respectively) were identified by ¹⁹F NMR and mass spectrometry and in the case of Ph₃TeF₂OH by X-ray crystallography Ph₃TeF₂OH has nonequivalent F atoms and the condition under which stereoselective F exchange occurs are known. The coordination about Te is octahedral with two Ph groups trans to each other and the third Ph trans to an F atom. The molecule exhibits the longest known Te(VI) F bond 2.011(2) Å. This same F which undergoes the more rapid exchange in solution is involved in H-bonding in the crystal, linking centrosymmetric related molecule into dimers where OH-F is 1.90(3) Å < O-H-F is 1.77(4) Å. However, H-bonding is not responsible for the stereoselective F exchange in solution²⁴⁵.

A series of phenyl tellurium(VI) fluoride PhTeF₅, Ph₃TeF₃, Ph₃TeF₂Cl, and Ph₄TeF₂ were prepared by oxidative fluorination of Te(IV) compounds with XeF₂. The compounds were characterized by elemental analysis, ¹⁹F and ¹²⁵Te NMR mass spectra²⁴⁶.

The reaction of TeMe₄ with XeF₂ in MeCN yielded the new compound cis-TeF₂Me₄ in 87% yield. Difluorotetramethyl tellurium(IV) has been charac-

terized by Mass spectroscopy, ^1H , ^{13}C , ^{19}F and ^{125}Te NMR spectra, methylation of TeF_2Me_4 with dimethyl zinc at reduced temperature proceed smoothly in diethyl ether to generate TeMe_6 in 68% yield. Hexamethyl tellurium is more thermally stable than TeMe_4 ²⁴⁷.

$(\text{CH}_3)_2\text{TeI}_4$ is triclinic, space group PI, with $a = 7.640(3)$, $b = 12.600(5)$, $c = 6.592(3)\text{\AA}$, $\alpha = 82.82(3)$, $\beta = 106.54(3)$ and $\gamma = 106.45(3)^\circ$, $d(\text{cald}) = 3.832$ for $Z = 2$. The structure was defined by least square to a final $R_1 = 0.061$. I-I bond ($2.748\text{--}3.456\text{\AA}$) and weak Te-I bonds ($2.809\text{--}3.957\text{\AA}$) and does not contain Te(IV) ²⁴⁸.

Some other organotellurium compounds which have not been included in the above discussion may be classified as below:

- (i) Tellurium ylides
- (ii) Heterocyclic tellurium compounds

(i) Tellurium ylides

This is a different group of organotellurium compounds. Sadekov prepared a number of tellurium ylides by reacting aryltellurium halides and 1,1-dimethyl 1 - 3, 5 - cyclohexanedione in boiling benzene containing triethylamine²⁴⁹⁻²⁵⁰.

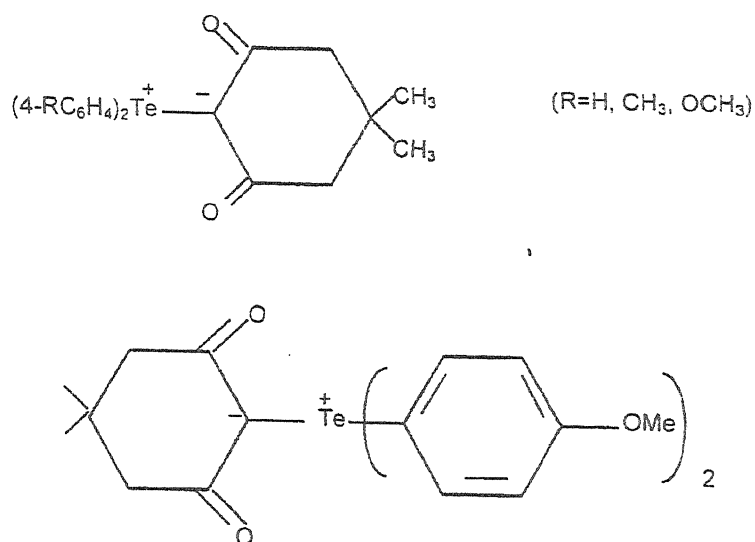


Fig. 34

The compound shown in Fig 35 synthesised by Freeman¹⁶ in 1970 is the only other tellurium ylide known .

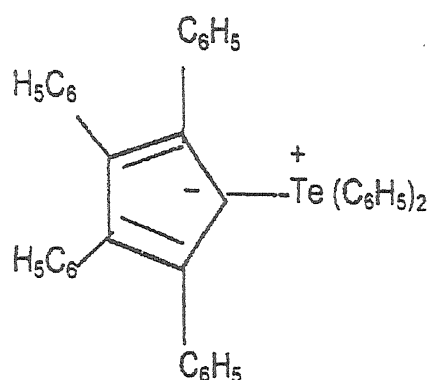


Fig. 35

(ii) Heterocyclic tellurium Compounds

New tellurium heterocyclic chemistry has been summarized²⁵¹. Telluraphthalic anhydrides (Fig.36) were obtained by treating NaBH₄ with Te followed by phthaloyl chloride²⁵². several five and six membered, 1,1-dihalogeno-1-tellura compounds have been prepared and their properties studied²⁵³⁻²⁵⁹. Treatment of sodium phenyl acetylide with tellurium in DMSO gave the ditellurols (Fig.37)²⁶⁰.

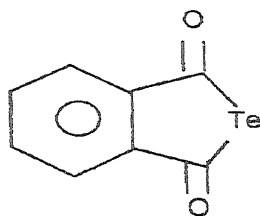


Fig. 36

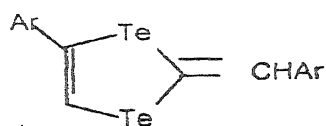


Fig. 37

When equimolar amounts of phenoxtelluride and its 10, 10-di-nitrate were dissolved in dichloromethane a solid (Fig.38) products separated²⁶¹.

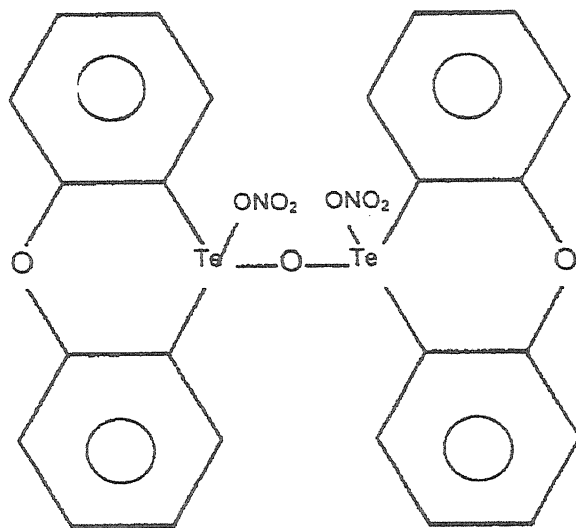
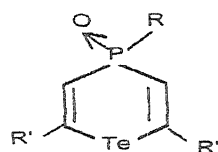
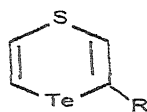


Fig. 38

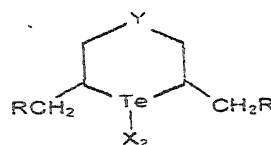
Some new heterocyclic tellurium rings synthesized are shown in Fig. 39 with references shown in brackets:



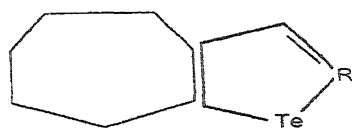
(Ref. 264)



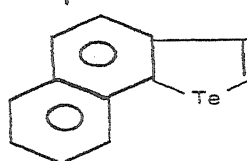
(Ref. 265)



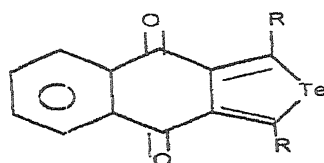
(Ref. 266)



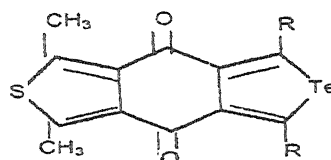
(Ref. 267)



(Ref. 267)



(Ref. 268)



(Ref. 268)

A review with 661 references mainly for 1981 of the chemical and properties of monocyclic thiophenes, benzofused thiophenes, thiophene analogous of polycyclic aromatic hydrocarbons, thiophene fused to 5- and 6- membered hetero-atomic ring selenophenes and tellurophenes is reported²⁶²⁻²⁶⁵.

In last few years some new organotellurium complexes have been synthesized. Cyclopentadienyl metal tellate (OTeF_6) complexes²⁶⁶. Reactions of $[\text{M}_2(\text{CO})_{10}]$ ($\text{M} = \text{Mn}$ or Re) with xenon bis [pentafluorooxo-tellurate (VI) and selenate (VI)]²⁶⁷, synthesis and characterization of monomeric telluro complexes of zinc and cadmium. Crystal and molecular structure of bis[2-(4,4-dimethyl-2-oxazoliny) phenyl] ditelluride,²⁶⁸ synthesis and characterization of Novel Chiral ortho-Tellurated complexes derived from (s) -1-(Dimethylamnio) ethyl Benzene. Crystal and Molecular structure of {2-[(S)-1-(Dimethyl amino)

ethyl] phenyl¹] tellurium trichloride²⁶⁹.

Synthesis, spectroscopic and structural studies on rhodium (I) and (III) and iridium (I) and (III) selenoether and telluroether complexes involving organometallic co-ligands²⁷⁰, synthesis and characterization of tris (trimethylsilyl) methylaluminium chalcogenides $[RAl(\mu_3-E)]_4$ ($R = (Me_3Si)_3C$; ($E = Se, Te$) and 1-Azaallylgallium chalcogenides $[R^1Ga(\mu_2-E)_2]$ ($R^1 = (Me_3Si)_2C(Ph)C(Me_3Si)N$; $E = S, Se, Te$)²⁷¹, bis (tetraisopropyl cyclopentadienyl nickel) dichalcogenid : complexes of the Novel $[CpME]_2$ Type ($E = S, Se, Te$)²⁷². Monooxytellurane (IV) derivatives ($\{10-Te-4(C_3O)\}$). Synthesis and molecular structure of triaryltelluronium carboxylate compounds²⁷³, organotellurium precursors for metal organic chemical vapour deposition (MOCVD) of mercury cadmium telluride (MCT)²⁷⁴. Stereochemical aspects of Tellurium complexes with sulfur ligands: Molecular compounds and supramolecular associations²⁷⁵.

A very few work have been done on organotellurium complexes with monocyclic ligands²⁷⁶⁻²⁸⁰.

A very few organotellurium compounds with schiff base ligands are known but the reaction of organotellurium compounds (R_2TeX_2) with 3 - mercapto - 4 - salicyldimino - 1,2,4 - triazole; 3 mercapto - 4 - β - isatinylimino - 1,2,4 - triazole and α - phenyl salicylaldimino - methyl - β - naphthol are not known.

The chapters in the thesis have been organized to provide an easy access to the formation available on the topics treated. The first two chapters deals with the general introduction of organotellurium compounds, materials used and the experimental techniques used to characterised and the synthesised compounds. In the third chapter the various organotellurium (IV) compounds of the type (R_2TeX_2) where $[(C_6H_5CH_2)_2TeI_2]$; $[(C_6H_4)_2TeCl_2]$; $[(p-MeOC_6H_4)_2TeCl_2]$; $[(p-Me_2NC_6H_4)C_6H_5TeCl_2]$; $[(p-Me_2NC_6H_4)(p-MeOC_6H_4)TeCl_2]$; $[(p-Me_2NC_6H_4)(p-EtOC_6H_4)TeCl_2]$; and $[(CH_3)TeI_2]$ 3-mercapto-4- salicyldimino - 1,2,4 - triazole have been studied. in the IV and V chapter

the various organometallic compounds of the type R_2TeX_2 (where - $[(C_6H_5CH_2)_2TeI_2]$; $[(C_6H_4)_2TeCl_2]$; $[(p-MeOC_6H_4)_2TeCl_2]$; $[(p-Me_2NC_6H_4)C_6H_5TeCl_2]$; $[(p-Me_2NC_6H_4)(p-MeOC_6H_4)TeCl_2]$; $[(p-Me_2NC_6H_4)(p-EtOC_6H_4)TeCl_2]$; and $[(CH_3)TeI_2]$ with 3-mercapto-4- β -isatinylimino - 1,2,4-triazole and with..... 1,2,4,-triazole respectively have been studied to establish reaction product geometry and structure.

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CHAPTER - II

STARTING MATERIALS, ANALYTICAL METHODS AND EXPERIMENTAL TECHNIQUES

This chapter deals with the source from where various starting materials have been obtained. There are several physico-chemical methods for the study of newly synthesized complexes are also given.

Materials

- (i) *Solvents* : E.Merck(L.R.Grade) and Ranbaxy solvents were used after purification and drying by conventional methods¹.
- (ii) *Tellurium Powder* : Finely divided tellurium powder received from Aldrich was used without further purification.
- (iii) *Tellurium tetrachloride* : Anhydrous tellurium tetrachloride was obtained from B.D.H. Other starting materials used in the present investigation, prepared either from reported methods or obtained from commercial sources as listed in table 1 and were used after purification.

Table1: Specifications and abbreviaton of materials employed.

Name	Source	Abbreviation
Salicylaldehyde	SISCO	-
Isatin	SISCO	-
β -naphtol	BDH	-
3-mercapto-4-amino 1,2,4-triazole	BDH	-
α -Phenyl-amino-methyl- β -naphtol	Aldrich	-

Experimental Techniques

A brief description of the techniques used in the investigation of the newly synthesised complexes described in the present work are given below:

1. Infrared Spectroscopy
2. Molar Conductivity Measurement
3. Elemental Analysis and
4. X-Ray Photoelectron Spectroscopy

When infrared light is passed through a sample of a compound, some of the frequencies are absorbed, while other frequencies are transmitted through the sample without being absorbed. If we plot the absorbance or transmittance against frequency, the result is an infrared spectrum. Infrared spectrum of all these complexes were recorded in KBr or CsI on a perkin Elmer 621 and /or 782 spectrophotometer.

$$\Lambda_m = \frac{\text{Cell constant} \times \text{conductance}}{\text{Concentration solute expressed in mol}^{-1} \text{ cm}^2}$$

Conventionally solution of 10^{-3} M strength are used for the conductance measurement. The electrical conductivities of 1×10^{-3} M solution in DMSO were obtained on digisun electronic conductivity bridge equilibrated at $25 \pm 0.1^\circ\text{C}$.

The chemical analysis is quite helpful in fixing the stoichiometric composition of the ligands as well as its complexes. Elemental analysis of C,H,N,O

and Te were carried out on semimicro scale at central Drug Research Institute, Lucknow, India.

The X-ray photoelectron spectra i.e. XPS were recorded on a VG scientific ESCA-3MKII electron spectrometer at National Chemical Laboratory, Pune-8. The Mg K α x-ray line (1253.6 eV) was used for photoexcitation. The Cu2P_{3/2} (BE = 932.8 \pm 0.2) and Au4f_{7/2} (BE = 83.8 \pm 0.1) lines were used to calibrate the instrument and Ag3d_{5/2} (BE = 368.2 eV) was used for cross-checking³. All the spectra were recorded using the same spectrometer parameter of 50 eV pass energy and 4 mm slit width. The reduced full width at half maximum (FWHM) at the Au4f_{7/2} (BE = 83.8 eV) level under these conditions was 1.2 eV.

The powdered sample was mixed with high purity silver powder to reduce the charging effect. A thin layer of such a sample was pressed in a gold metal gauze which was welded to nickel sample holder. The Ag3d_{5/2} level (BE = 368.2 eV) obtained from this sample was sharp and did not show any observable shift. Thus the changing of the the sample if at all present was negligible. The spectra were recorded in triplicate in the region of the interest. In the most of cases the binding energies were reproducible within \pm 0.1 eV.

Preparation of (C₆H₅CH₂)₂TeI₂

A mixture of benzylchloride (2.53g, 0.02 mol, tellurium powder (1.26 g, 0.01 mol and sodium iodide (3g, 0.02 mol) was heated under reflux at 110° C

for 40 hrs. The reaction mixture was extracted with dry chloroform, the chloroform extract concentrated and the residue recrystallised from chloroform-pet ether⁴.

Preparation of $(C_6H_4)_2TeCl_2$

0.125 mol of biphenyl (19.25g) was heated with 0.100 mol $TeCl_4$ (26.89g). At 110°C HCl was evolved. The reaction was continued between 140-160°C till HCl ceased to evolved (~18hrs). The solid thus obtained was washed several times with pet-ether (60-80°C) to remove excess reactants and the product was recrystallised from dry acetone⁵.

Preparation of Bis(p-methoxyphenyl) telluriumdihalide ($p-MeOC_6H_4)_2TeCl_2$

Tellurium tetrachloride (22.5g; 0.08 mol) and anisole (45.0 g; 0.4, 0.41 mol) were heated for 6 hrs at 160°C and the mixture was concentrated under reduced pressure to crystallization. The dichloride was recrystallized from cold acetonitrile⁷.

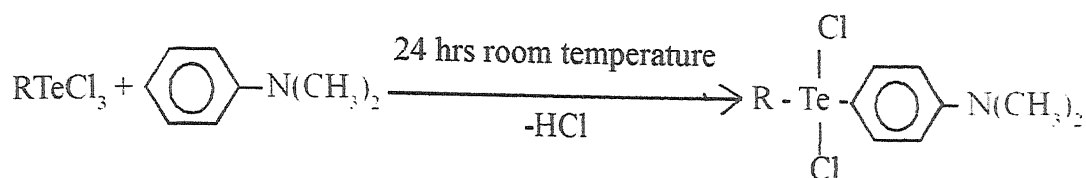
Yield = 27.5 g; 80%

m.p. = 182 - 83° [Reported (182 - 183°)]

Preparation of p-dimethylaminophenyl(aryl) tellurium dihalides ($p-Me_2NC_6H_4$)RTeCl₂:

The title compounds were prepared by mixing aryltellurium trichloride

with dimethylaniline at room temperature according to the following equation⁸.



(R = *p*-CH₃OC₆H₄, *p* - C₂H₅OC₆H₄)

Preparation of [(*p*-Me₂NC₆H₄)(*p*-MeOC₆H₄)]Te and [*p*-Me₂NC₆H₄](*P*-EtOC₆H₄)]Te :

p-dimethylaminophenyl(*p*-methoxyphenyl) telluride and *p*-dimethylaminophenyl (*p*-ethoxyphenyl) telluride were similarly prepared by reduction of corresponding dichlorides and had m.p. 96°c (reported 96-97°c) and 126°c (reported 126-127°c)^{9,8}.

yield = 100%

Preparation of dimethyltellurium diiodide(CH₃)₂TeI₂

In a glass bulb of 150-200 ml capacity, was sealed a mixture of 10.0g (0.07 mol) of amorphous tellurium and 22.4g (0.15mol) of methyl iodide. The sealed bulb, was kept in a water bath at 80°c for 36-48 hrs. The brittle red mass thus obtained, was powdered and extracted with chloroform. The mixture was filtered through a hot funnel to separate unreacted tellurium. The yield of dimethyltelluriumdiiodide based on the amount of crystalline solid obtained from the chloroform solution, was about 53% It was recrystallized from a nonaqueous solvent such as chloroform, benzene or acetone¹⁰.

Yield = 17.0g(53%)

m.p. = 127°(d)[Reported 127°(d)]

Preparation of p-dimethylaminopheny(p-methoxy phenyl tellurium dichloride (p-Me₂NC₆H₄) (p-MeOC₆H₄)TeCl₂:

p - methoxyphenyl tellurium trichloride (34.0g, 0.10mol) was intimately mixed with N, N - dimethylamine (36.0g, 0.30 mol). The reaction was exothermic, and a transient bluish green colour appeared. After 24 hrs the mixture was extracted several times with methanol, leaving a yellow crystalline residue of the dichloride. The product was recrystallised from methanol or benzene/methanol as yellow prism⁵.

Yield=32g(75%)

m.p. = 169-170°c[reported 170-172°c]

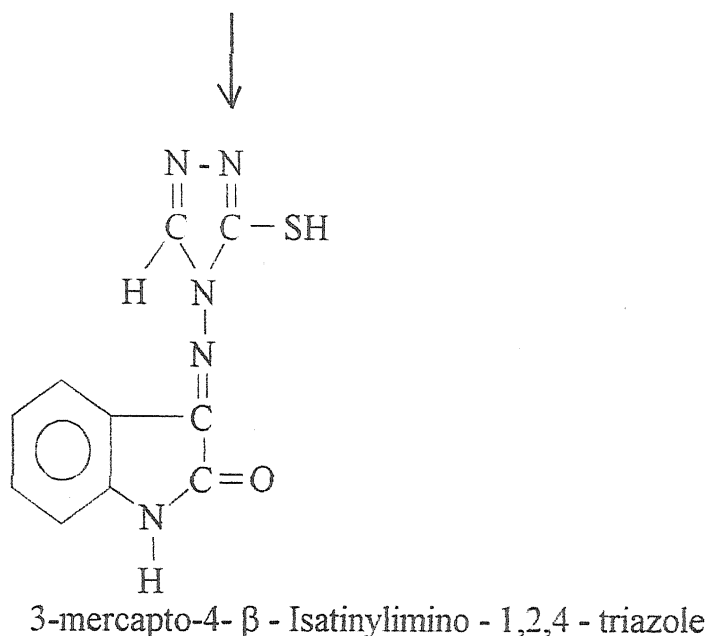
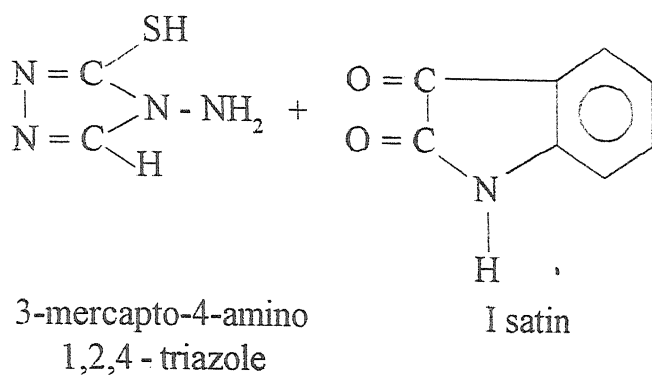
Preparation of [(p-Me₂NC₆H₄)(p-EtOC₆H₄)]TeCl₂:

It was prepared similarly⁸.

m.p. = 149-150°c[reported 153-154°c]

Preparation of 3-mercapto-4-β-Isatinylimino-1,2,4-triazole :

The compound is formed by refluxing 3-mercapto-4-amino-1,2,4-triazole with molar proportion of isatin in aqueous methanol.



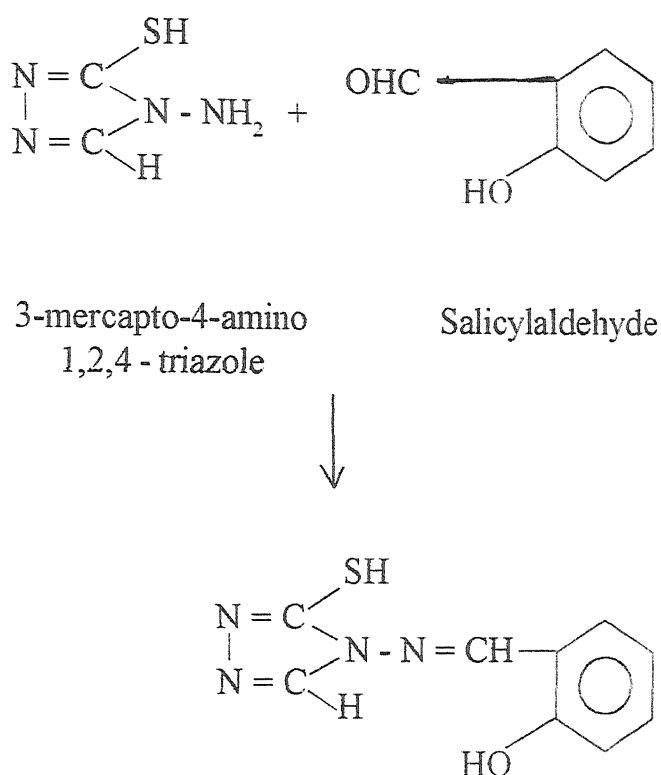
Procedure

About 11.6g of 3-mercapto-4-amino-1,2,4-triazole was dissolved in 50-60ml not aqueous methanol and treated with 14.8 g of isatin dissolved in 50-60 ml methanol. The resulting solution was refluxed for one hour when cream yellow product separated gradually. The product was collected on a filter, washed with aqueous methanol and dried in air. The Schiff base of isatin obtained from 4-amino-triazole is less soluble in methanol or ethanol but dissolves appreciably in pyridine and dioxane. The lignad is highly soluble in DMF. The product obtained by recrystallisation it with methanol. It was found to contain N =

28.41%. The title product required N = 28.3%

Preparation fo 3-mercapto-4-salicylaldimino-1,2,4-triazole:

The comound was prepared by condensing 3-mercapto-4-amino-1,2,4-triazole with equimolecular proportion of salicylaldehyde in aqueous methanol.



Procedure

3-mercapto-4- Salicylaldimino - 1,2,4 - triazole

About 11.6g of mercapto-4-amino-1,2,4-triazole was refluxed with 12.2g of salicylaldehyde in 60-70ml aqueous methanol containing 2-3ml glacial acetic acid for one hour. On refluxing, a clear solution was formed within 5-10 minutes from which crystallined needles separated gradually. The refluxate on cooling at room temperature deposited cream coloured product. The product was collected on a filter and recrystallsised with dioxan-methanol mixture. The

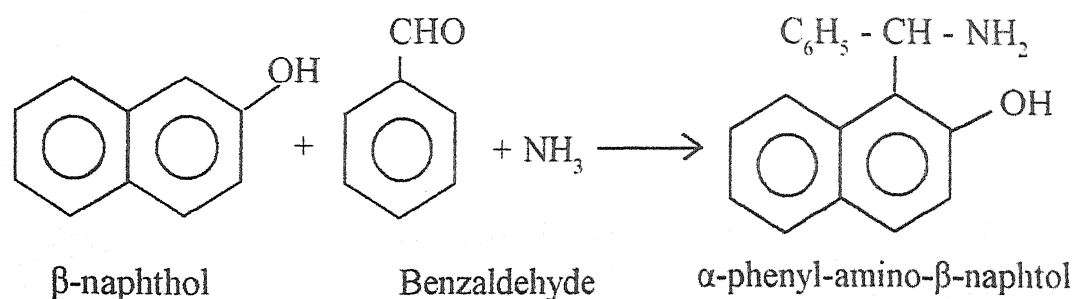
recrystallised product was collected on a filter, washed with methanol and dried in a desiccator over CaCl_2 . the product on analyse was found to contain N=25.34% The title product requires N=25.45%.

3-mercapto-4-salicylaldimino-5-methyl-1,2,4-triazole i.e.(5Me-salmtrH₂) and 3-mercapto-4-salicylaldimino-5 phenyl-1,2,4-triazole i.e.(5Ph-salmtrH₂) were prepared by same method as for 3-mercapto-4-salicyladimino-1,2,4-triazole; by taking 3-mercapto-4-amino-5methyl 1,2,4-triazole and 3-mercapto-4-amino-5phenyl 1,2,4-triazole respectively.

Preparation of α -phenylsalicylaldimino-methyl- β -naphthol:

The compound was prepared in two steps by reported method:

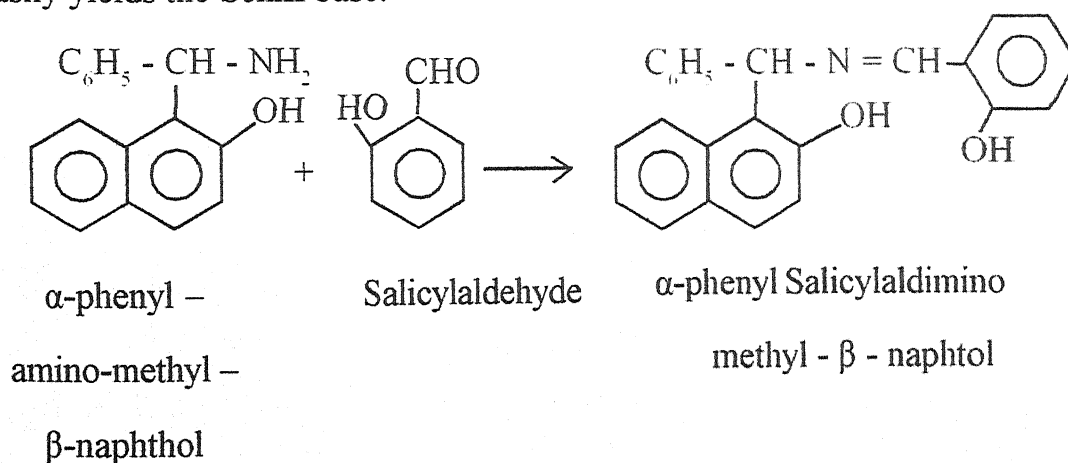
- (a) Preparation of α -phenyl-amino-methyl- β -naphthol.
- (b) Condensation of α -phenyl-amino-methyl- β -naphthol with Salicylaldehyde.
- (c) Condensation of α -phenyl-aminomethyl- β -naphthol with salicylaldehyde.
- (d) α -phenyl-aminomethyl- β -naphthol was prepared by reacting β -naphthol with benzaldehyde and ammonia in hot ethanol.



Procedure

About 21.2 g of freshly distilled benzaldehyde was dissolved in 50 ml ethanol. Crystalline 28.8 g β -naphthol was dissolved in 150 ml hot methanol and taken in a three-necked 500 ml round bottom flask fitted with a mechanical stirrer. The solution was maintained at 90-95° and ethanolic solution of benzaldehyde and conc. ammonia (30 ml) were added dropwise from separating funnel to β -naphthol solution. The addition of reactants was completed in half an hour while maintaining the temperature to 90-95°C and stirring the reaction mixture with mechanical stirrer. When the addition of benzaldehyde and ammonia was complete the resulting solution was refluxed for 4 hours on steam bath. After refluxing the volume of refluxate was reduced to ¼ by distilling the alcohol as a steam bath. The concentrated solution was mixed with 500 ml of cold water when white product separated. It was collected on a filter. The residue was dried and extracted with ether the product obtained on evaporation of ether was recrystallised with ethanol. M.P. Found : 244°C.

(b) Condensation of salicylaldehyde with α -phenyl -aminomethyl - β -naphthol easily yields the Schiff base.



Procedure

About 12.2g salicyldehyde was dissolved in 20-30ml ethanol and added to ethanolic solution of 25g of α -phenyl-aminomethyl- β -naphthol dissolved in 50ml hot ethanol. The resulting solution was treated with 2ml glacial acetic acid and refluxed on steam bath for an hour when light yellow product separated. The product was collected on a filter and washed with ethanol. Found N= 3.81% and required for titled product N=3.96%.

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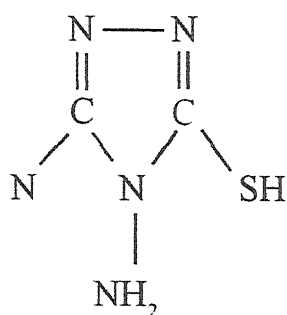
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CHAPTER – III

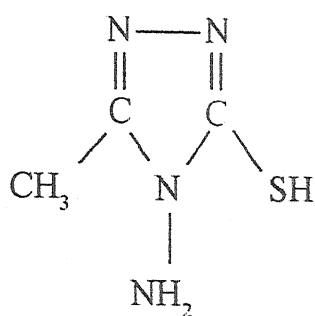
“COMPLEXES OF
 R_2TeX_2 WITH 3 -
MERCAPTO - 4 -
SALICYLALDIMINO -
1, 2, 4 - TRIAZOLE”

**“COMPLEXES OF R_2TeX_2 WITH 3 - MERCAPTO - 4 -
SALICYLALDIMINO -1, 2, 4 - TRIAZOLE”**

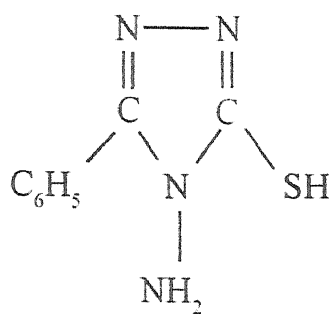
3-Mercapto-4-amino-1,2,4-triazole(I) is potential 'N' and 'S' donor ligand and its complexes with transition metals are well known¹⁻⁵. The methyl derivatives 5-methyl-3-mercapto-4-amino-1,2,4-triazole(ii) and 5-phenyl-3 mercapto-4-amino-1,2,4- triazole (III) have same donor sites similar to parent ligand(I).



(I)

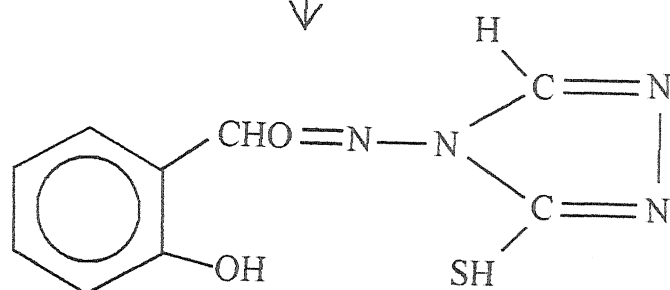
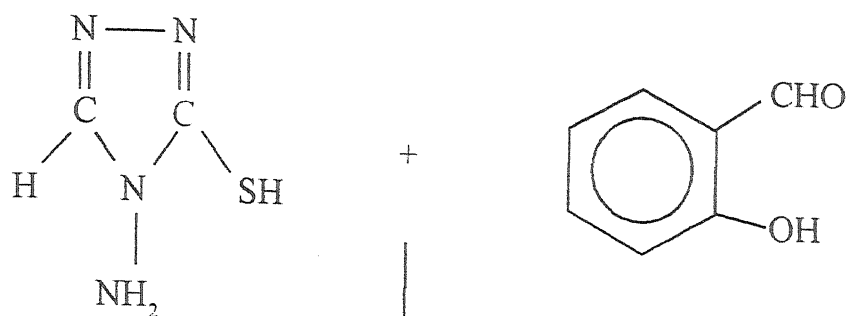


(II)

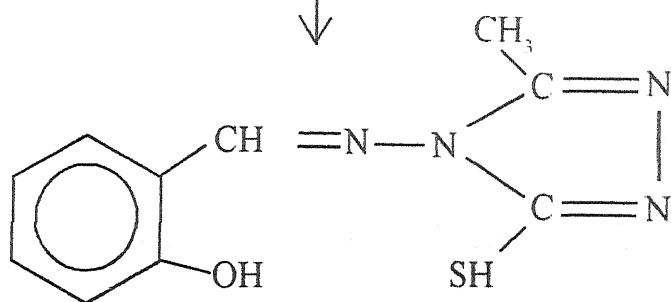
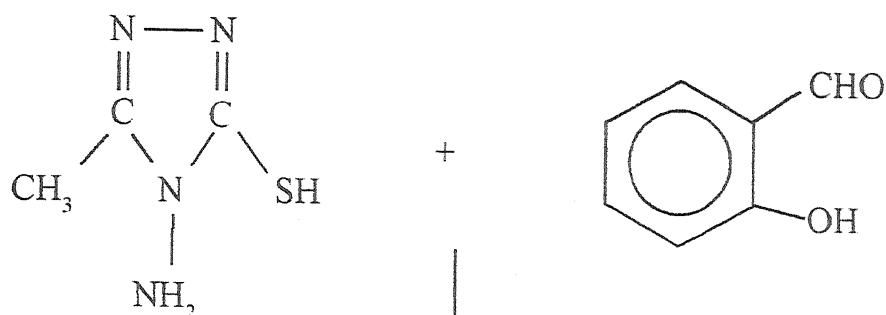


(III)

The NH_2 group of these triazole derivatives condenses with aldehyde or Ketone and forms Schiff base ligands with salicylaldehyde.

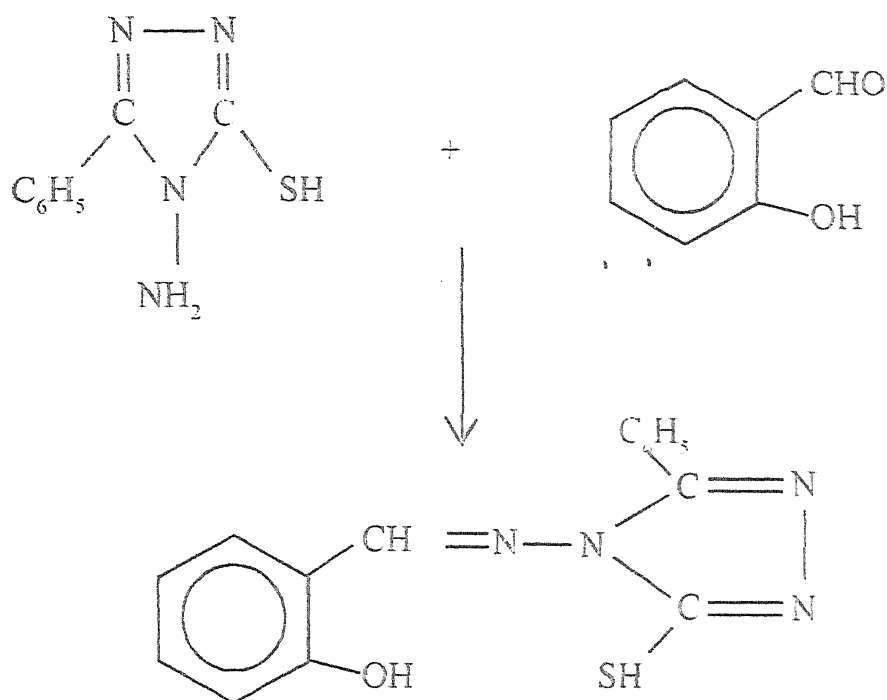


3 - mercapto - 4 - salicylaldimino - 1, 2, 4 - triazole
i.e. abbreviated as (SalmtrH₂)



Schiff Base

5 - methyl - 3 - mercapto - 4 - salicylaldimino - 1, 2, 4 - triazole
i.e. (5 - Me - SalmtrH₂)



Schiff Base

5 - phenyl - 3 - mercapto - 4 - salicylaldimino - 1, 2, 4 - triazole
i.e. (5 - Ph - SalmtrH₂)

Although various Schiff base ligands interaction with R_2TeX_2 have been studied, to know the geometry and significance of the produced complexes, the interaction of R_2TeX_2 with salmtrH₂ and its derivatives Schiff base ligands have been not studied, to know the site of coordination and geometry. This chapter deals with such type of study.

Preparation of $[R_2Te(salmtr)]$, $R_2Te(5-Me-salmtr)$ and $[R_2Te(5-Ph-salmtr)]$ complexes:

The R_2TeX_2 (1mmol) i.e. $[(C_6H_5CH_2)_2TeI_2]$; $[(C_6H_4)_2TeCl_2]$; $[(p-MeOC_6H_4)_2TeCl_2]$; $[(p-Me_2NC_6H_4)PhTeCl_2]$; $[(p-Me_2NC_6H_4)(p-$

MeOC₆H₄)TeCl₂]; [(*p*-Me₂NC₆H₄)(*p*-EtOC₆H₄)TeCl₂] and [(CH₃)₂TeI₂] was dissolved in dry methanol (30ml) and Schiff base ligand i.e. salmtrH₂ or 5-Me-salmtrH₂ or 5-Ph-salmtrH₂ (1mmol) was mixed in this solution. The mixture was refluxed for 3-4 hrs. The solid product was obtained filtered product was washed with pet-ether and air dried.

Preparation of [R₂Te(salmtrH)₂] R₂Te(5-Me-salmtrH)₂] and [R₂Te(5-Ph-salmtrH)₂] complexes:

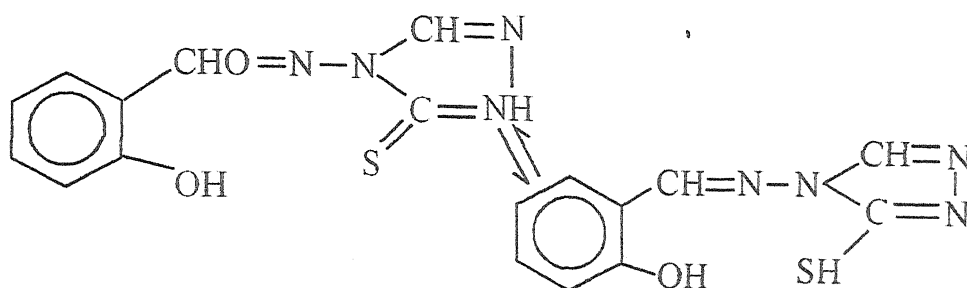
The R₂TeX₂ (1mmol) i.e. [(C₆H₅CH₂)₂TeI₂]; [(C₆H₄)₂TeCl₂]; [(*p*-MeOC₆H₄)₂TeCl₂]; [(*p*-Me₂NC₆H₄)PhTeCl₂]; [(*p*-Me₂NC₆H₄)(*p*-MeOC₆H₄)TeCl₂]; [(*p*-Me₂NC₆H₄)(*p*-EtOC₆H₄)TeCl₂] and [(CH₃)₂TeI₂] was dissolved in dry methanol (40ml) and Schiff base ligand salmtrH₂ or 5-Me-salmtrH₂ or 5-Ph-salmtrH₂ (2mmol) was mixed in this solution. The mixture was refluxed for two hrs. The solid product was obtained filtered washed with pet-ether and air dried.

RESULTS AND DISCUSSION

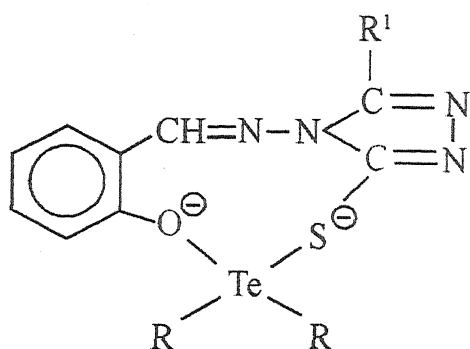
The all prepared complexes – [R₂Te(salmtr)]; [R₂Te(5-Me-salmtr)]; [R₂Te(5-Ph-salmtr)]; [R₂Te(salmtrH)₂]; [R₂Te(5-Me-salmtrH)₂] and [R₂Te(5-Ph-salmtrH)₂] were found to be air stable. The observed molar conductance values of all the complexes in acetone were observed 20-30 ohm⁻¹ cm² mol⁻¹ indicate that they all are non-electrolyte in nature (Table 2).

The IR spectra of 3-mercapto 4-salicylaldimino-1,2,4,-triazole i.e.

(salmtrH₂) contains a phenolic OH and a mercapto sulphur capable of existing in Ketoenol tautomeric form:-

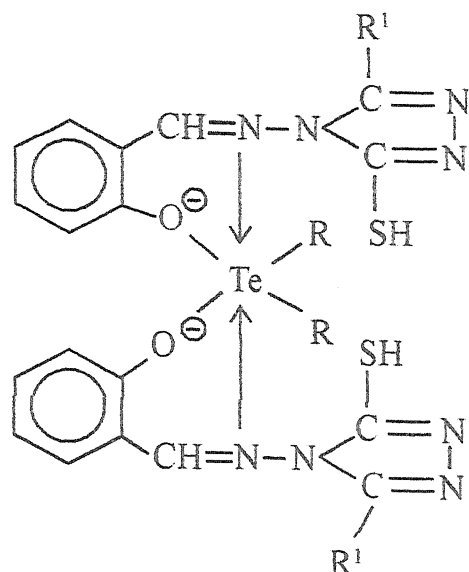


The IR bands position of ligand salmtrH₂ are listed in table the ligand displays a medium band at 3230 cm⁻¹ assignable to $\nu(\text{OH})$ of phenolic hydroxygroup and sharp band at 3115 cm⁻¹ attributable to $\nu\text{N-H}$ group. The absence of $\nu\text{S-H}$ in the region 2400-2850 cm⁻¹ indicate that ligands exclusively exists in thion tautomer rather than thiol form. The free ligand displays $\nu\text{C=N}$ aldimino part at 1615 cm⁻¹. The $\nu\text{C=N}$ vibration is shifted to higher frequency



$\text{R}^1 = \text{H, Me, Ph}$

Structure of $[\text{R}_2\text{Te}(\text{Salmtr})]$, $[\text{R}_2\text{Te}(5\text{-Me-Salmtr})]$
and $[\text{R}_2\text{Te}(5\text{-Ph-Salmtr})]$ complexes



$R^1 = \text{H, Me, Ph}$

Structure of $[\text{R}_2\text{Te}(\text{SalmtrH})_2]$, $[\text{R}_2\text{Te}(5 - \text{Me} - \text{SalmtrH})_2]$
and $[\text{R}_2\text{Te}(5 - \text{Ph} - \text{SalmtrH})_2]$ complexes

and observed as broad and strong bands due to mixing of $\text{UC}=\text{N}$ of triazole ring . The thioamide band I of free ligand is observed at 1536 cm^{-1} , Thioamide band II is observed at 1342 cm^{-1} . The $\delta(\text{OH})$ of free ligand is assigned to a bond at 1320 cm^{-1} . The UC-O phenolic group is assigned to a band at 1145 cm^{-1} . The thiomide bands III and IV of free ligand are attributed to IR bands at 1232 and 940 cm^{-1} .

Table 1 : IR spectral bands of ligand *SalmtrH*₂

<i>Band Position</i>	<i>Assignments</i>
3250 m	VOH
3115 a	VNH
3060 w	UCH Phenyl group

Continue of Table 1.....

2980 w	ν CH side chain
1635 s	ν CN+ ν C=C
1568 m	Phenyl ring skeletal
1536 s	δ NH+thiomide I
1482 m	<div style="display: inline-block; vertical-align: middle; font-size: 3em; line-height: 1;">[</div> δ NH ring+phenyl ring skeletal vibration thiomide band II
1445 vs	
1342 s	
1320 w	δ OH phenolic
1278 va	ν C-N
1232 m	thiomide band III
1215 s	ν C-C
1200 s	ν N-N
1145 m	ν C-O
1125 s	phenyl and triazole ring ν C-C and ν C-N band
1050 s	
1030 m	
962 s	
940 vs	thioamide band IV
820 s	phenyl ring (C-H) and triazole ring (N-H) and (C-H) out of plane bending band phenyl ring and
805 vs	
758 s	
730 s	
700 m	

Continue of Table 1.....

660 a	triazole ring deformation
610 m	vibrations + thioamide
578 s	group deformation
540 w	vibrations
490 m	
465 m	
430 w	
375 w	
278 m	

W = weak ; m= medium; s= strong; vs = very strong

The $\nu_{\text{C=N}}$ frequency of $[\text{R}_2\text{Te}(\text{salmtr})]$, $[\text{R}_2\text{Te}(5\text{-Me-salmtr})]$ and $[\text{R}_2\text{Te}(5\text{-Ph-salmtr})]$ complex have shown bands at $1655\text{-}1632\text{-}1\text{ cm}^{-1}$ which was same as in their Schiff base ligand, suggesting noninvolvement of nitrogen atom group of ν_{C} in coordination. But the $\nu_{\text{C=N}}$ frequency band in $[\text{R}_2\text{Te}(\text{salmtrH})_2]$, $[\text{R}_2\text{Te}(5\text{-Me-salmtrH})_2]$ and $[\text{R}_2\text{Te}(5\text{-Ph-salmtrH})_2]$ complexes have shown at $1620\text{-}1610\text{ cm}^{-1}$ which normally appeared at $1655\text{-}1632\text{ cm}^{-1}$ in their Schiff base ligands, suggesting involvement of $\nu_{\text{C=N}}$ group, nitrogen to the tellurium metal ion. The $\delta(\text{OH})$ of free ligand is assigned to a band at 1320 cm^{-1} , disappeared in all these prepared complexes. The $\nu_{\text{C-O}}$ phenolic group is assigned to a band at 1145 cm^{-1} which shifts to higher wave number and observed around $1350\text{-}1370\text{ cm}^{-1}$.

In $[\text{R}_2\text{Te}(\text{salmtr})]$, $[\text{R}_2\text{Te}(5\text{-Me-salmtr})]$ and $[\text{R}_2\text{Te}(5\text{-Ph-salmtr})]$

complexes.

The thioamide bands which appear in free ligand attributed at 1232 and 940 cm^{-1} the former band shifts to higher wave number and latter move around 820-840 cm^{-1} . The major shift of thioamide band (which appear at 940 cm^{-1}) in the complexes is attributed to deprotonation of thiol SH and bonding of thioamide group through deprotonated thio sulphur atom of the ligand molecule. But in $[\text{R}_2\text{Te}(\text{salmtrH})_2]$, $[\text{R}_2\text{Te}(5\text{-Te-salmtrH})_2]$ and $[\text{R}_2\text{Te}(5\text{-Ph-salmtrH})_2]$ complexes the thioamide bands which appears at 1232 and 940 cm^{-1} in the free ligand have shown no change suggesting non-involvement of SH group in the complexation. In far IR $\nu\text{Te-C}$ was observed 560-540 cm^{-1} in all these prepared complexes The $\nu\text{Te-X}$ were absent in all these prepared complexes.

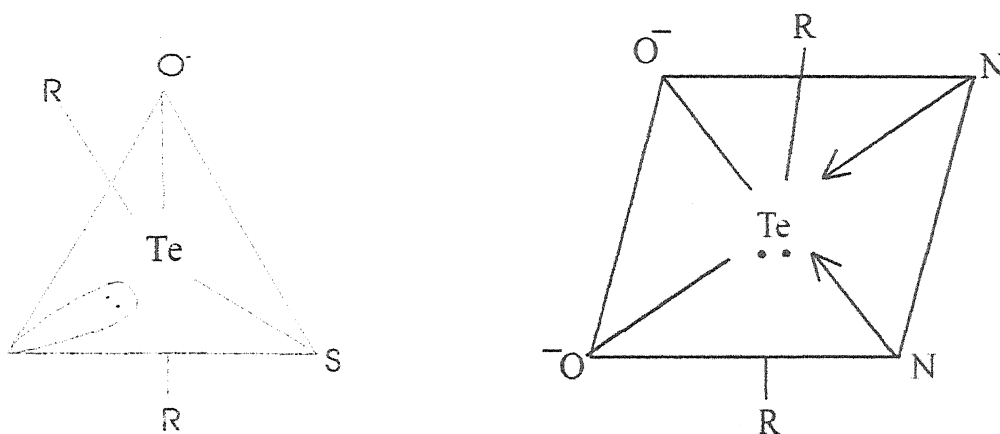
The X-ray photoelectron spectra data for $\text{Te}3d_{3/2, 5/2}$, N1s, O1s and 2p are listed in table 3. It was noticed that $\text{Te}3d_{3/2, 5/2}$ binding energy value decrease with respect to their R_2TeX_2 ; suggesting increase of electron density on tellurium metal ion due to coordination. (Fig 1 to 7).

In complexes $[\text{R}_2\text{Te}(\text{salmtr})]$ $[\text{R}_2\text{Te}(5\text{-Me-salmtr})]$ and $[\text{R}_2\text{Te}(5\text{-ph-salmtr})]$ O_{1s} and s2p binding energy values were observed more than their respective Schiff base ligand suggesting involvement of oxygen and sulphur atom in the complexation. But during the analysis of N1s binding energy data, it was observed, no change in BE value with respect to their respective Schiff base ligand. Suggesting noninvolvement of nitrogen (of $\nu\text{C=N}$ gp) in the complexation⁸. (Fig. 8)

During the study of $[R_2Te(salmtrH)_2]$, $[R_2Te(5-Me-salmtrH)_2]$, and $[R_2Te(5-Ph-salmtrH)_2]$, it was observed that O1s and N1s binding energies values were increase with respect to their respective Schiff base lignd, while S2p binding energy values were observed same as in ligand. These observations concluded the involuement of nitrogen and oxygen atom, not sulphur atom in the complexation of these complexes (Fig 10).

Further it was noticed that all these prepared complexes have not shown X2p (X = Cl or I) photoelectron peak, suggesting their absence in the complexes.

On the badis of elemental analysis, molar conductivity IR and XPS data , the geometry of these complexes can be concluded and as shown in fig. i.e. trigonal bipyramidal in $[R_2Te(Samtr)]$ and Pseudooctahedral in $[R_2Te(SamtrH)_2]$ complexes.



Geometry of $[R_2Te(Samtr)]$ and $[R_2Te.(SamtrH)]$

Table-3 $Te3d_{3/2}$, $5/2$; $N1s$, $O1s$ and $S2p$ binding energies(eV) in R_2TeX_2 , $[R_2Te(salmtr)_2]$ and $[R_2Te(salmtrH)_2]$ complexes.

Sr.No.	Ligand and Complexes	Te metal ion		N1s	O1s	S2P
		$Te3d_{3/2}$	$Te3d_{5/2}$			
1.	SalmtrH ₂	-	-	399.4	532.4	165.2
2.	5-Me- SalmtrH ₂	-	-	399.4	532.4	165.2
3.	5-Ph- SalmtrH ₂	-	-	399.4	532.4	165.2
4.	(C ₆ H ₅ CH ₂) ₂ TeI ₂	585.8	575.4	-	-	-
5.	[(C ₆ H ₅ CH ₂) ₂ Te(Salmtr)]	584.2	574.2	-	534.6	166.4
6.	[(C ₆ H ₅ CH ₂) ₂ Te(5MeSalmtr)]	584.2	574.2	-	534.6	166.4
7.	[(C ₆ H ₅ CH ₂) ₂ Te(5Ph-Salmtr)]	584.2	574.2	-	534.6	166.4
8.	[(C ₆ H ₅ CH ₂) ₂ Te(SalmtrH) ₂]	584.2	574.2	402.8	534.6	-
9.	[(C ₆ H ₅ CH ₂) ₂ Te(5Me-SalmtrH) ₂]	584.2	574.2	402.8	534.6	-
10.	[(C ₆ H ₅ CH ₂) ₂ Te(5Ph-SalmtrH) ₂]	584.2	574.2	402.8	534.6	165.2
11.	[(C ₆ H ₄) ₂ TeCl ₂]	585.6	575.2	-	-	-
12.	[(C ₆ H ₄) ₂ Te(Salmtr)]	584.2	574.0	399.4	534.6	166.4
13.	[(C ₆ H ₄) ₂ Te(5Me-Salmtr)]	584.2	574.0	399.4	534.6	166.4
14.	[(C ₆ H ₄) ₂ Te(5Ph-Salmtr)]	584.2	574.0	399.4	534.6	166.4
15.	[(C ₆ H ₄) ₂ Te(SalmtrH) ₂]	584.2	574.0	402.6	534.6	165.2

Continue of Table 3

16.	$[(C_6H_4)_2Te(SalmtrH)_2]$	584.2	574.0	402.6	534.6	165.2
17.	$[(C_6H_4)_2Te(SalmtrH)_2]$	584.2	574.0	402.6	534.6	165.2
18.	$[p-MeOC_6H_4)_2TeCl_2]$	585.6	575.6	-	-	-
19.	$[p-MeOC_6H_4)_2Te(Salmtr)]$	584.2	574.0	399.4	534.6	166.4
20.	$[p-MeOC_6H_4)_2Te(5Me-Salmtr)]$	584.2	574.0	399.4	534.6	166.4
21.	$[p-MeOC_6H_4)_2Te(5Ph-Salmtr)]$	584.2	574.0	399.4	534.6	166.4
22.	$[p-MeOC_6H_4)_2Te(SalmtrH)_2]$	584.2	574.0	402.6	534.6	165.2
23.	$[p-MeOC_6H_4)_2Te(5Me-SalmtrH)_2]$	584.2	574.0	402.6	534.6	165.2
24.	$[p-MeOC_6H_4)_2Te(5Ph-SalmtrH)_2]$	584.2	574.0	402.6	534.6	165.2
25.	$[p-Me_2NC_6H_4)(C_6H_5)TeCl_2]$	585.6	575.6	-	-	-
26.	$[p-Me_2NC_6H_4)(C_6H_5)Te(salmtr)]$	584.4	574.2	399.4	534.6	166.4
27.	$[p-Me_2NC_6H_4)(C_6H_5)Te(5Me-salmtr)]$	584.4	574.2	399.4	534.6	166.4
28.	$[p-Me_2NC_6H_4)(C_6H_5)Te(5Ph-salmtr)]$	584.4	574.2	399.4	534.6	166.4
29.	$[p-Me_2NC_6H_4)(C_6H_5)Te(salmtrH)_2]$	584.4	574.2	402.6	534.6	165.2
30.	$[p-Me_2NC_6H_4)(C_6H_5)Te(5Me-salmtrH)_2]$	584.4	574.2	402.6	534.6	165.2
31.	$[p-Me_2NC_6H_4)(C_6H_5)Te(5Ph-salmtrH)_2]$	584.4	574.2	402.6	534.6	165.2
32.	$[p-Me_2NC_6H_4)(p-MeOC_6H_4)TeCl_2]$	585.8	575.4	-	-	-
33.	$[p-Me_2NC_6H_4)(p-MeOC_6H_4)Te(salmtr)]$	584.2	574.0	399.4	534.6	166.4
34.	$[p-Me_2NC_6H_4)(p-MeOC_6H_4)Te(5Me-salmtr)]$	584.2	574.0	399.4	534.6	166.4
35.	$[p-Me_2NC_6H_4)(p-MeOC_6H_4)Te(5Ph-salmtr)]$	584.2	574.0	399.4	534.6	166.4

Continue of Table 3

36.	$[(p\text{-Me}_2\text{NC}_6\text{H}_4)(p\text{-MeOC}_6\text{H}_4)\text{Te(salmtrH)}_2]$	584.2	574.0	402.8	534.6	165.2
37.	$[(p\text{-Me}_2\text{NC}_6\text{H}_4)(p\text{-MeOC}_6\text{H}_4)\text{Te(salmtrH)}_2]$	584.2	574.0	402.8	534.6	165.2
38.	$[(p\text{-Me}_2\text{NC}_6\text{H}_4)(p\text{-MeOC}_6\text{H}_4)\text{Te(salmtrH)}_2]$	584.2	574.0	402.8	534.6	165.2
39.	$[(p\text{-Me}_2\text{NC}_6\text{H}_4)(p\text{-EtOC}_6\text{H}_4)\text{TeCl}_2]$	585.4	575.6	-	-	-
40.	$[(p\text{-Me}_2\text{NC}_6\text{H}_4)(p\text{-EtOC}_6\text{H}_4)\text{Te(salmtr)}]$	584.2	574.2	399.4	534.6	166.4
41.	$[(p\text{-Me}_2\text{NC}_6\text{H}_4)(p\text{-EtOC}_6\text{H}_4)\text{Te(5Me salmtr)}]$	584.2	574.2	399.4	534.6	166.4
42.	$[(p\text{-Me}_2\text{NC}_6\text{H}_4)(p\text{-EtOC}_6\text{H}_4)\text{Te(5Ph-salmtr)}]$	584.2	574.2	399.4	534.6	166.4
43.	$[(p\text{-Me}_2\text{NC}_6\text{H}_4)(p\text{-EtOC}_6\text{H}_4)\text{Te(salmtrH)}_2]$	584.2	574.2	402.8	534.6	165.2
44.	$[(p\text{-Me}_2\text{NC}_6\text{H}_4)(p\text{-EtOC}_6\text{H}_4)\text{Te(5Me salmtrH)}_2]$	584.2	574.2	402.8	534.6	165.2
45.	$[(p\text{-Me}_2\text{NC}_6\text{H}_4)(p\text{-EtOC}_6\text{H}_4)\text{Te(5Ph-salmtrH)}_2]$	584.2	574.2	402.8	534.6	165.2
46.	$(\text{CH}_3)_2\text{TeI}_2$	585.6	575.8	-	-	-
47.	$[(\text{CH}_3)_2\text{Te(salmtr)}]$	584.2	574.2	399.4	534.6	166.4
48.	$[(\text{CH}_3)_2\text{Te(5Me salmtr)}]$	584.2	574.2	399.4	534.6	166.4
49.	$[(\text{CH}_3)_2\text{Te(5Ph-salmtr)}]$	584.2	574.2	399.4	534.6	166.4
50.	$[(\text{CH}_3)_2\text{Te(salmtrH)}_2]$	584.2	574.2	402.8	534.6	165.2
51.	$[(\text{CH}_3)_2\text{Te(5Me salmtrH)}_2]$	584.2	574.2	402.8	534.6	165.2
52.	$[(\text{CH}_3)_2\text{Te(5Ph-salmtrH)}_2]$	584.2	574.2	402.8	534.6	165.2

Table 2:- Elemental and molar conductivity data of $[R_2Te(salmtr)]$ and $[R_2Te(salmtrH)_2]$ complexes.

Sr. No.	Complexes	Elemental analysis				Molar conductivity $ohm^{-1} cm^2 mol^{-1}$
		Te	C	H	N	
1.	$[(C_6H_5CH_2)_2Te(Salmtr)]$	25.4 (25.6)	55.2 (55.4)	3.2 (3.6)	5.2 (5.6)	20
2.	$[(C_6H_4)_2Te(Salmtr)]$	27.0 (27.1)	53.4 (53.6)	2.8 (2.9)	5.8 (5.9)	22
3.	$[p-MeOC_6H_4)_2Te(Salmtr)]$	25.4 (25.5)	55.0 (55.2)	4.2 (4.0)	5.6 (5.6)	24
4.	$[p-Me_2NC_6H_4)C_6H_5Te(salmtr)]$	24.4 (24.8)	53.2 (53.6)	4.0 (4.0)	8.2 (8.1)	26
5.	$[p-Me_2NC_6H_4)(p-MeOC_6H_4)Te(salmtr)]$	23.2 (23.4)	53.4 (53.8)	4.0 (4.2)	7.4 (7.7)	18
6.	$[p-Me_2NC_6H_4)(p-EtOC_6H_4)Te(salmtr)]$	22.4 (22.8)	53.4 (53.7)	4.2 (4.2)	7.4 (7.5)	16
7.	$[(CH_3)_2Te(salmtr)]$	36.6 (36.7)	37.4 (37.9)	3.2 (3.4)	8.0 (8.0)	23

Continue of Table 2

8.	$[(C_6H_5CH_2)_2Te(5-Me\ Salmtr)]$	24.8 (24.8)	56.2 (56.0)	4.2 (4.2)	5.4 (5.4)	24
9.	$[(C_6H_4)_2Te(5-Me\ Salmtr)]$	26.2 (26.4)	54.4 (54.6)	3.0 (3.3)	5.4 (5.8)	26
10.	$[p-MeOC_6H_4)_2Te(5-Me\ Salmtr)]$	24.1 (24.0)	54.2 (54.3)	4.0 (4.1)	5.0 (5.2)	28
11.	$[p-MeNC_6H_4)C_6H_5Te(5-Me\ Salmtr)]$	22.8 (22.9)	51.4 (51.7)	4.1 (4.1)	12.4 (12.5)	24
12.	$[p-Me_2NC_6H_4)(p-MeOC_6H_4)Te(5Me\ Salmtr)]$	22.4 (22.8)	53.6 (53.7)	4.2 (4.4)	7.2 (7.5)	20
13.	$[p-Me_2NC_6H_4)(p-EtOC_6H_4)Te(5Me-Salmtr)]$	22.0 (22.2)	54.2 (54.4)	4.6 (4.7)	7.2 (7.3)	16
14.	$[(CH_3)_2Te(5-Me-Salmtr)]$	35.4 (35.8)	40.2 (40.4)	4.0 (3.9)	7.4 (7.8)	18
15.	$[(C_6H_5CH_2)_2Te(5Ph-Salmtr)]$	26.8 (26.8)	52.4 (52.1)	5.2 (5.0)	5.4 (5.8)	16
16.	$[(C_6H_4)_2Te(5Ph-Salmtr)]$	23.2 (23.4)	59.4 (59.4)	3.4 (3.2)	5.4 (5.1)	16
17.	$[p-MeOC_6H_4)_2Te(5-Ph\ Salmtr)]$	20.2 (20.0)	55.2 (55.4)	3.8 (3.8)	4.2 (4.4)	20

Continue of Table 2

18.	$[(p\text{-MeNC}_6\text{H}_4)\text{C}_6\text{H}_5\text{Te}(5\text{-Ph SalmtrH})_2]$	24.4 (24.2)	43.2 (43.2)	4.3 (4.7)	8.0 (7.9)	26
19.	$[(p\text{-Me}_2\text{NC}_6\text{H}_4)(p\text{-MeOC}_6\text{H}_4)\text{Te}(5\text{-Ph Salmtr})]$	20.2 (20.5)	58.4 (58.0)	4.2 (4.3)	6.6 (6.7)	22
20.	$[(p\text{-Me}_2\text{NC}_6\text{H}_4)(p\text{-EtOC}_6\text{H}_4)\text{Te}(5\text{-Ph salmtr})]$	23.8 (23.8)	69.2 (69.5)	5.4 (5.4)	7.6 (7.8)	15
21.	$[(\text{CH}_3)_2\text{Te}(5\text{-Ph Salmtr})]$	30.0 (30.1)	48.0 (48.1)	3.6 (3.8)	6.5 (6.6)	20
22.	$[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{Te}(\text{SalmtrH})_2]$	18.2 (18.4)	55.2 (55.5)	4.1 (4.0)	8.1 (8.0)	22
23.	$[(\text{C}_6\text{H}_5)_2\text{Te}(\text{SalmtrH})_2]$	19.2 (19.3)	54.2 (54.4)	3.2 (3.3)	8.2 (8.4)	24
24.	$[(p\text{-MeOC}_6\text{H}_4)_2\text{Te}(\text{SalmtrH})_2]$	17.4 (17.6)	53.2 (53.0)	3.8 (3.9)	7.6 (7.7)	26
25.	$[(p\text{-MeOC}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{Te}(\text{salmtrH})_2]$	18.2 (18.0)	54.2 (54.3)	4.0 (4.1)	9.4 (9.9)	14
26.	$[(p\text{-Me}_2\text{NC}_6\text{H}_4)(p\text{-MeOC}_6\text{H}_4)\text{Te}(\text{salmtrH})_2]$	17.2 (17.3)	53.4 (53.8)	4.0 (4.2)	9.2 (9.5)	18
27.	$[(p\text{-Me}_2\text{NC}_6\text{H}_4)(p\text{-EtOC}_6\text{H}_4)\text{Te}(\text{salmtrH})_2]$	16.8 (16.9)	54.2 (54.4)	4.2 (4.4)	9.2 (9.3)	20

Continue of Table 2

28.	$[(CH_3)_2Te(salmtrH)_2]$	23.4 (23.6)	44.2 (44.4)	3.6 (3.7)	10.2 (10.4)	22
29.	$[(C_6H_5CH_2)_2Te(5-Me\ SalmtrH)_2]$	17.6 (17.7)	56.4 (56.7)	4.2 (4.4)	7.6 (7.8)	12
30.	$[(C_6H_4)_2Te(5-Me\ SalmtrH)_2]$	18.2 (18.5)	55.6 (55.7)	3.6 (3.8)	8.0 (8.1)	10
31.	$[p-MeOC_6H_4)_2Te(5-Me\ SalmtrH)_2]$	16.8 (16.9)	54.2 (54.3)	4.0 (4.2)	7.2 (7.4)	18
32.	$[p-MeOC_6H_4)C_6H_5Te(5-Me\ SalmtrH)_2]$	17.0 (17.3)	55.2 (55.5)	4.8 (4.9)	9.4 (9.5)	16
33.	$[p-Me_2NC_6H_4)(p-MeOC_6H_4)Te(5-Me\ SalmtrH)_2]$	16.4 (16.7)	54.4 (54.9)	4.2 (4.6)	9.0 (9.2)	14
34.	$[p-Me_2NC_6H_4)(p-EtOC_6H_4)Te(5-Me\ SalmtrH)_2]$	16.2 (16.4)	55.2 (55.5)	4.6 (4.8)	8.4 (8.9)	22
35.	$[(CH_3)_2Te(5-Me\ SalmtrH)_2]$	22.2 (22.4)	46.4 (46.5)	4.0 (4.2)	9.4 (9.8)	22
36.	$[(C_6H_5CH_2)_2Te(5-Ph\ SalmtrH)_2]$	15.0 (15.1)	62.4 (62.6)	4.0 (4.3)	6.3 (6.6)	24
37.	$[(C_6H_4)_2Te(5-Ph\ SalmtrH)_2]$	15.6 (15.7)	61.8 (61.9)	3.4 (3.6)	6.4 (6.8)	26

Continue of Table 2

38.	$[(p\text{-MeOC}_6\text{H}_4)_2\text{Te}(5\text{-Ph SalmtrH})_2]$	14.2 (14.6)	60.2 (60.3)	4.0 (4.1)	6.2 (6.4)	20
39.	$[(p\text{-MeOC}_6\text{H}_4)\text{C}_6\text{H}_5\text{Te}(5\text{-Ph SalmtrH})_2]$	14.4 (14.9)	61.2 (61.5)	4.2 (4.3)	8.0 (8.2)	22
40.	$[(p\text{-Me}_2\text{NC}_6\text{H}_4)(p\text{-MeOC}_6\text{H}_4)\text{Te}(5\text{-Ph SalmtrH})_2]$	14.2 (14.3)	60.2 (60.8)	4.1 (4.3)	7.6 (7.8)	24
41.	$[(p\text{-Me}_2\text{NC}_6\text{H}_4)(p\text{-EtOC}_6\text{H}_4)\text{Te}(5\text{-Ph SalmtrH})_2]$	14.0 (14.1)	61.0 (61.1)	4.4 (4.5)	7.2 (7.7)	28
42.	$[(\text{CH}_3)_2\text{Te}(5\text{-Ph SalmtrH})_2]$	18.2 (18.4)	55.2 (55.5)	4.0 (4.0)	8.0 (8.0)	26

Te3d_{3/2} photoelectron peak.

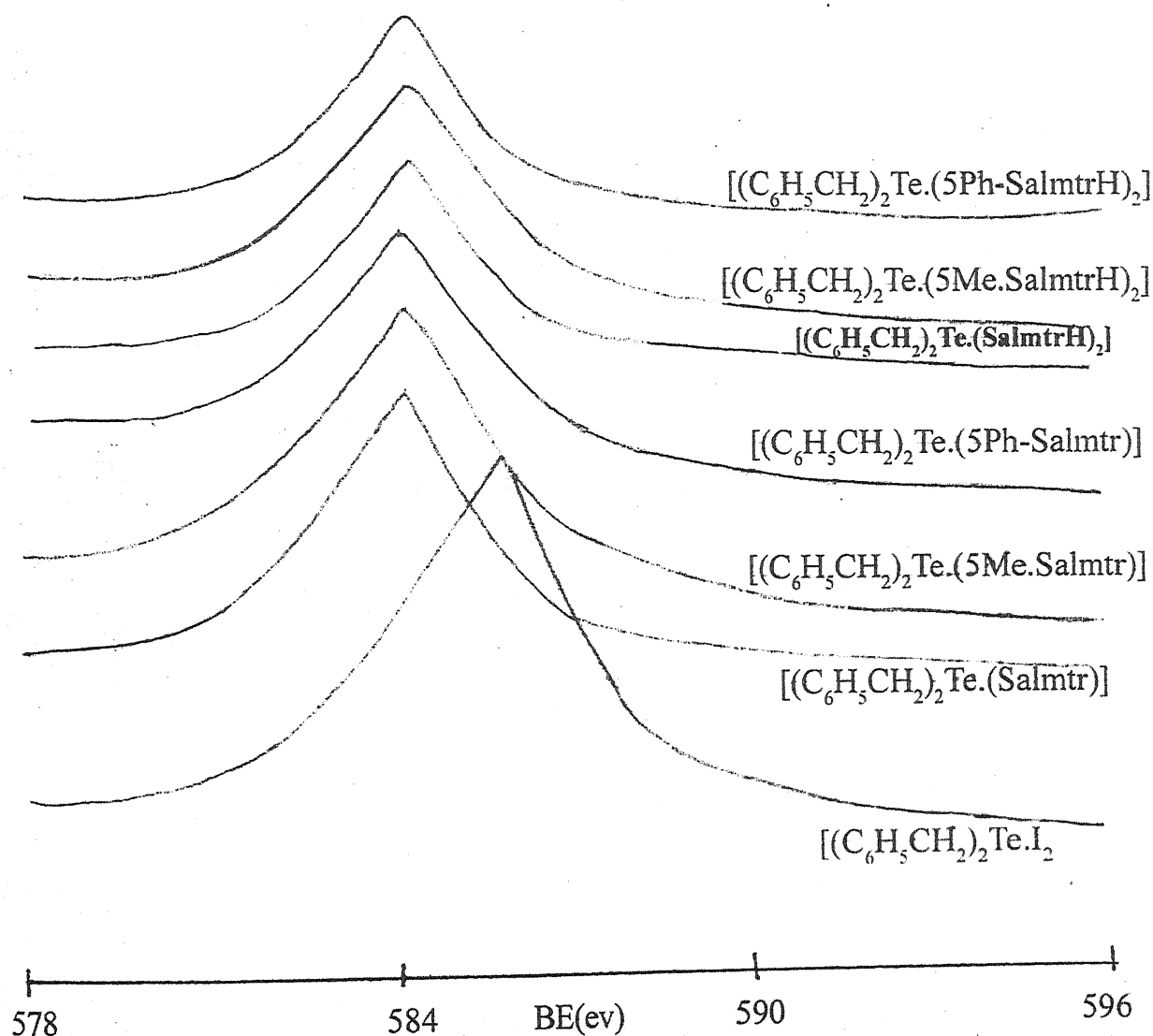


Fig 1 : Te 3d_{3/2} binding energies (ev) in $(C_6H_5CH_2)_2 Te I_2$
 $[(C_6H_5CH_2)_2 Te(Salmtr)]$ and $[(C_6H_5CH_2)_2 Te.(SalmtrH)_2]$

Te3d_{3/2} photoelectron peak.

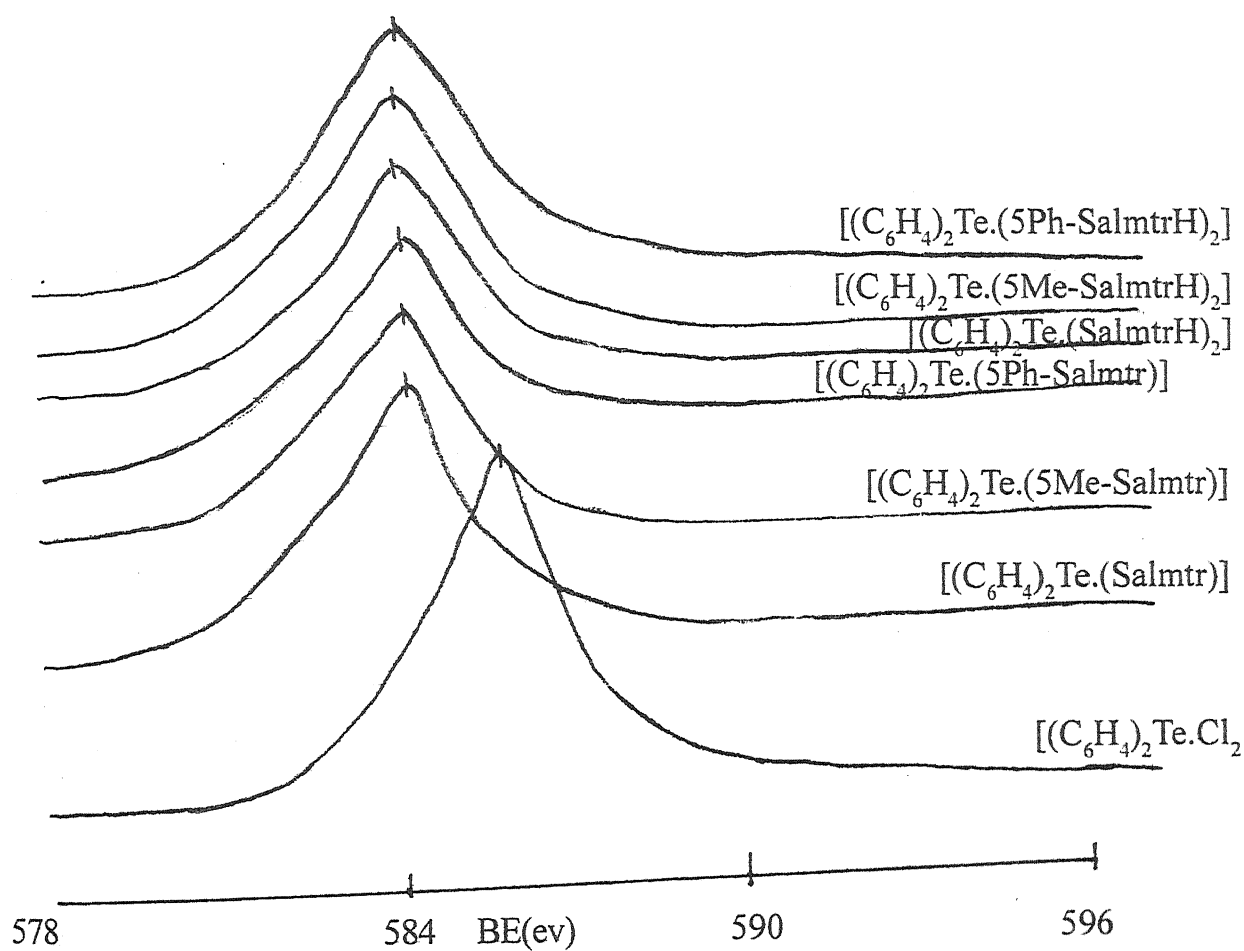


Fig 2 : Te 3d_{3/2} binding energies (ev) in $(C_6H_4)_2Te.Cl_2$, $[(C_6H_4)_2Te.(Salmtr)]$ and $[(C_6H_4)_2Te.(SalmtrH)_2]$

Te3d_{3/2} photoelectron peak.

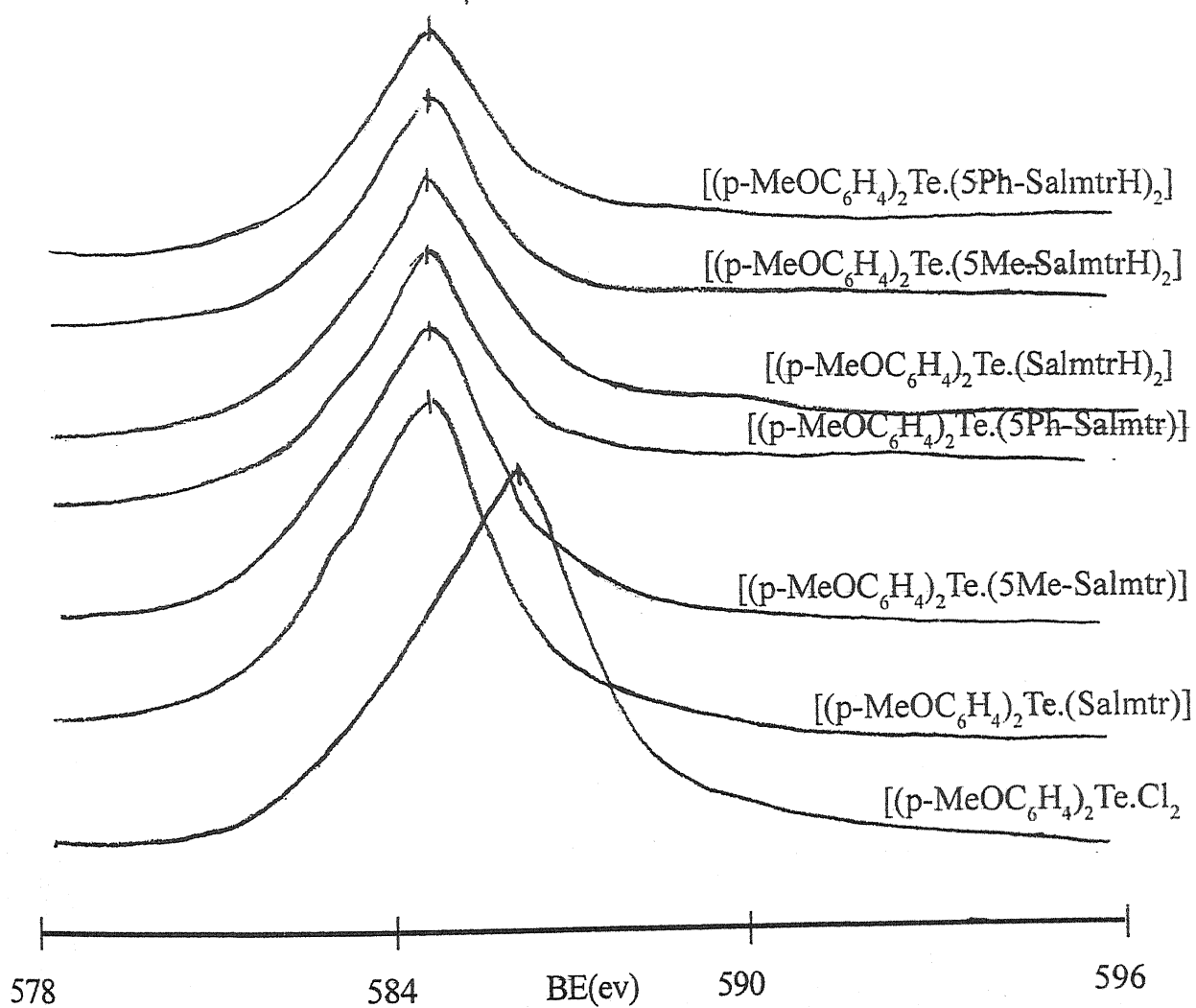


Fig 3 : Te 3d_{3/2} binding energies (ev) in $[(p\text{-MeOC}_6\text{H}_4)_2\text{Te} \cdot \text{Cl}_2]$, $[(p\text{-MeOC}_6\text{H}_4)_2\text{Te} \cdot (\text{Salmtr})]$ and $[(p\text{-MeOC}_6\text{H}_4)_2\text{Te} \cdot (\text{SalmtrH})_2]$

Te3d_{3/2} photoelectron peak.

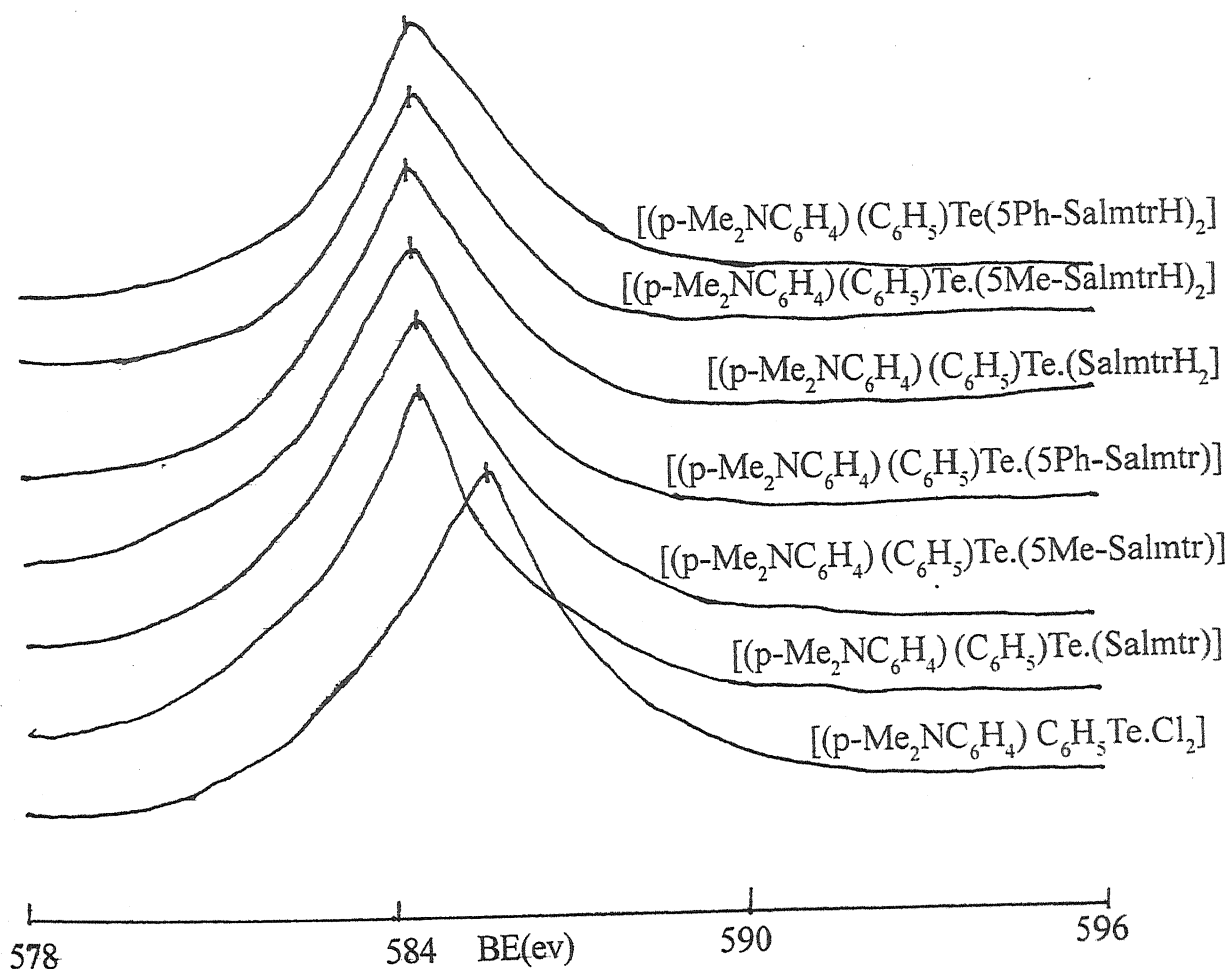


Fig 4 : Te 3d_{3/2} binding energies (ev) in $[(p\text{-Me}_2\text{NC}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{Te}(\text{Cl}_2)]$, $[(p\text{-Me}_2\text{NC}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{Te}(\text{Salmtr})]$ and $[(p\text{-Me}_2\text{NC}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{Te}(\text{SalmtrH})_2]$

Te3d_{3/2} photoelectron peak.

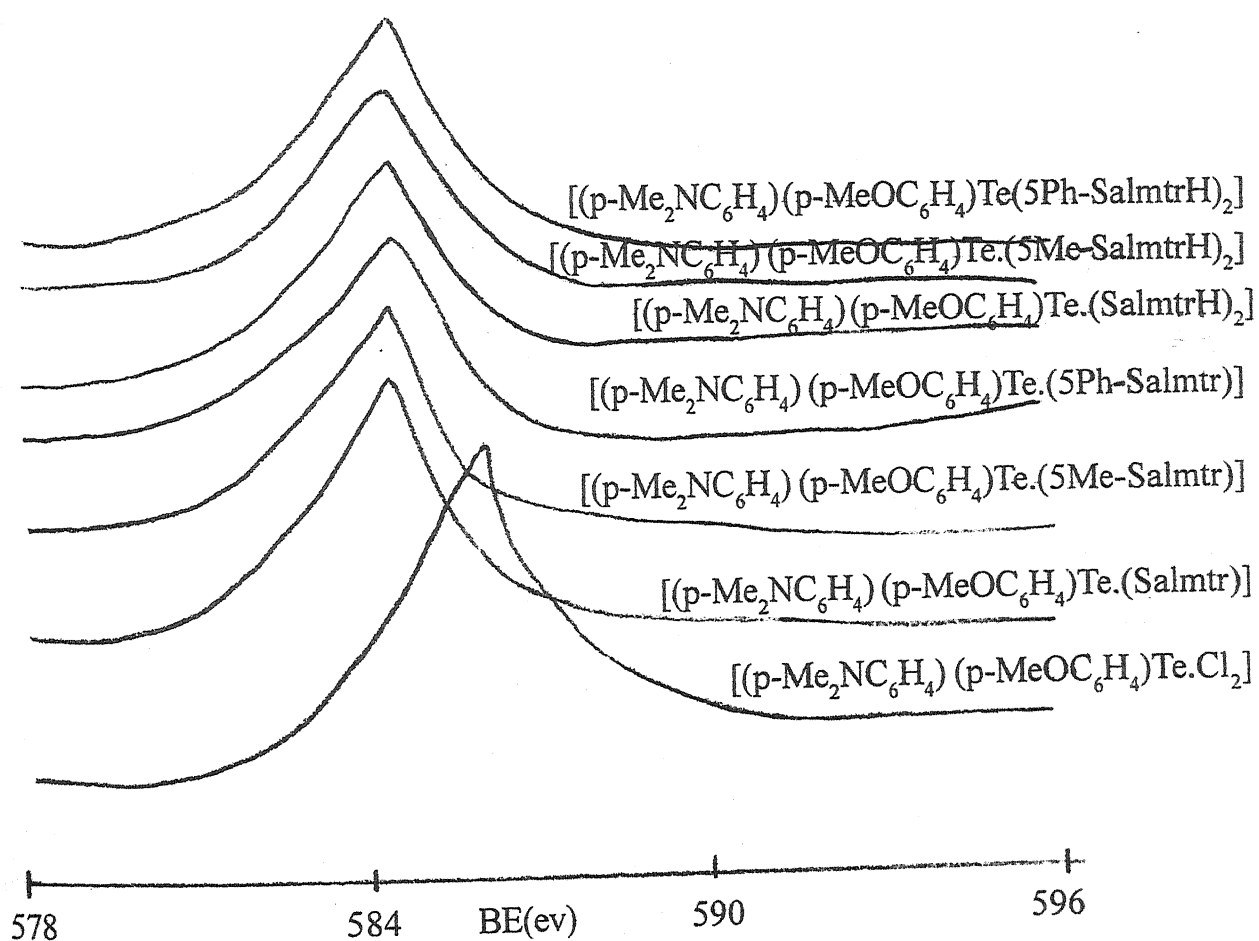


Fig 5 : Te 3d_{3/2} binding energies (ev) in $[(p\text{-Me}_2\text{NC}_6\text{H}_4)(p\text{-MeOC}_6\text{H}_4)\text{Te.Cl}_2]$; $[(p\text{-Me}_2\text{NC}_6\text{H}_4)(p\text{-MeOC}_6\text{H}_4)\text{Te}(\text{Salmtr})]$ and $[(p\text{-Me}_2\text{NC}_6\text{H}_4)(p\text{-MeOC}_6\text{H}_4)(\text{SalmtrH})_2]$

Te3d_{3/2} photoelectron peak.

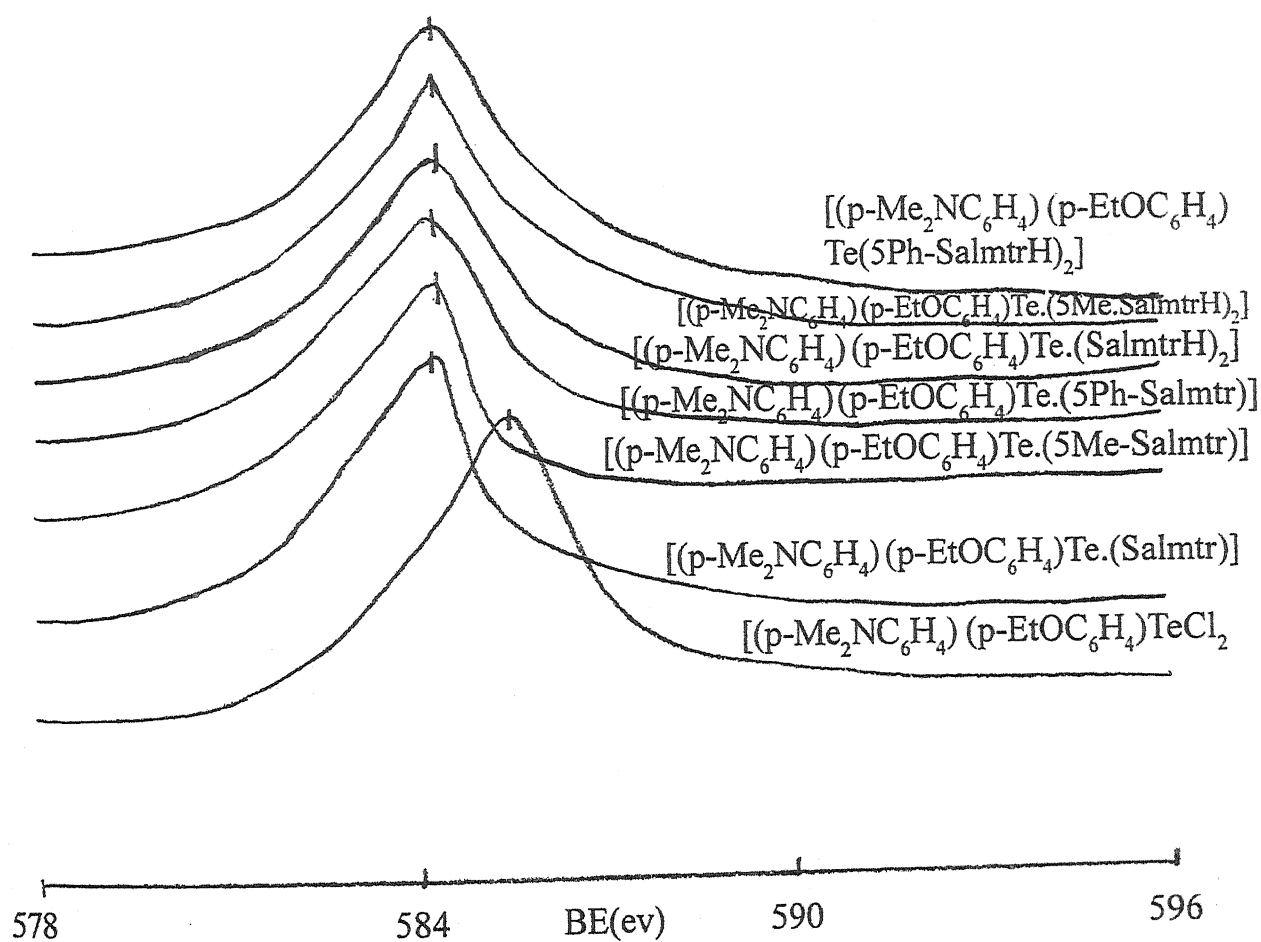


Fig 6 : Te 3d_{3/2} binding energies (ev) in [(p-Me₂NC₆H₄) (p-EtOC₆H₄) Te Cl₂]
 [(p-Me₂NC₆H₄) (p-EtOC₆H₄) Te(Salmtr)]
 and [(p-Me₂NC₆H₄) (p-EtOC₆H₄) Te.(SalmtrH)₂]

Te3d_{3/2} photoelectron peak.

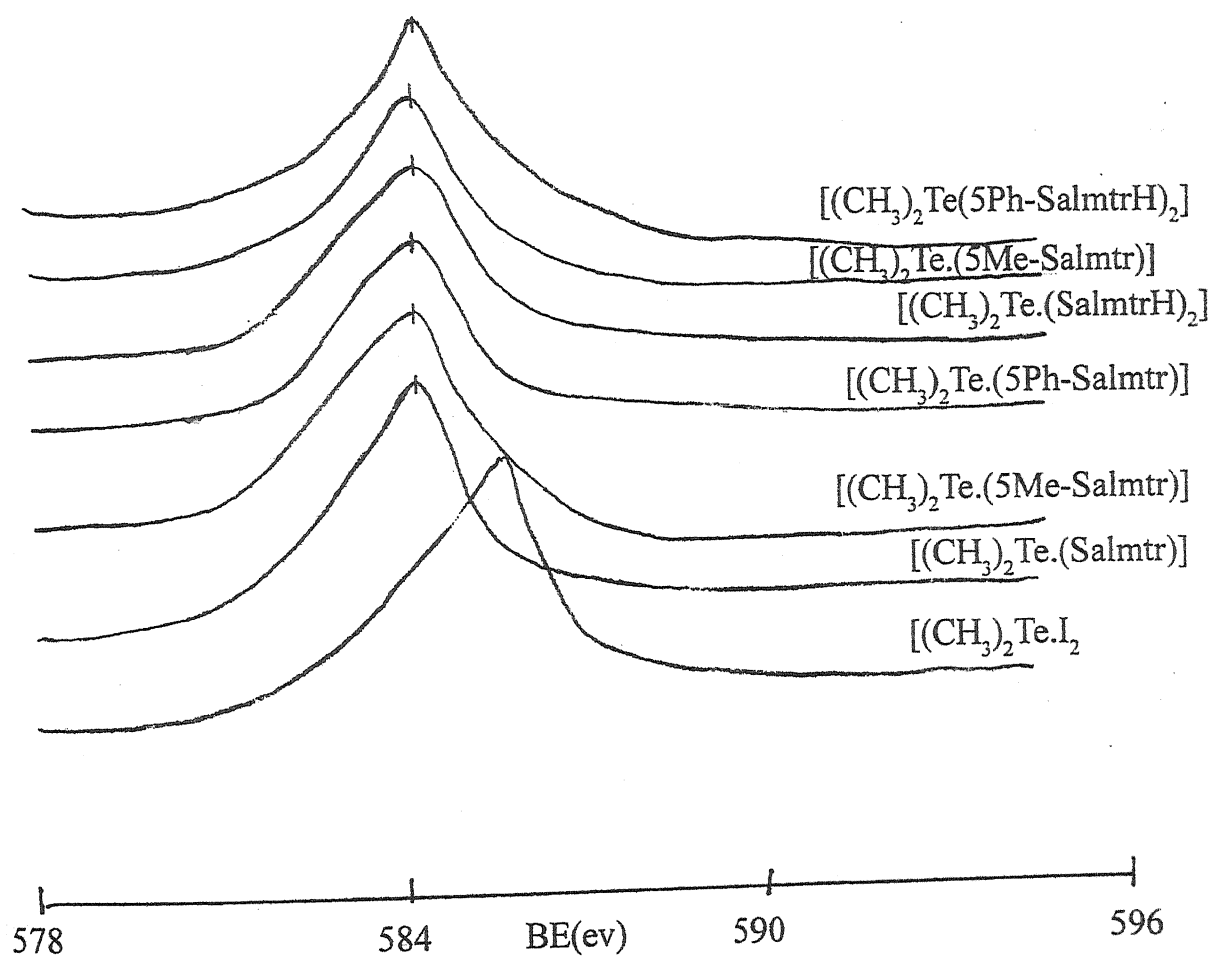


Fig 7 : Te 3d_{3/2} binding energies (ev) in $[(CH_3)_2TeI_2]$; $[(CH_3)_2Te(Salmtr)]$ and $[(CH_3)_2Te.(SalmtrH)_2]$

N1s photoelectron peak

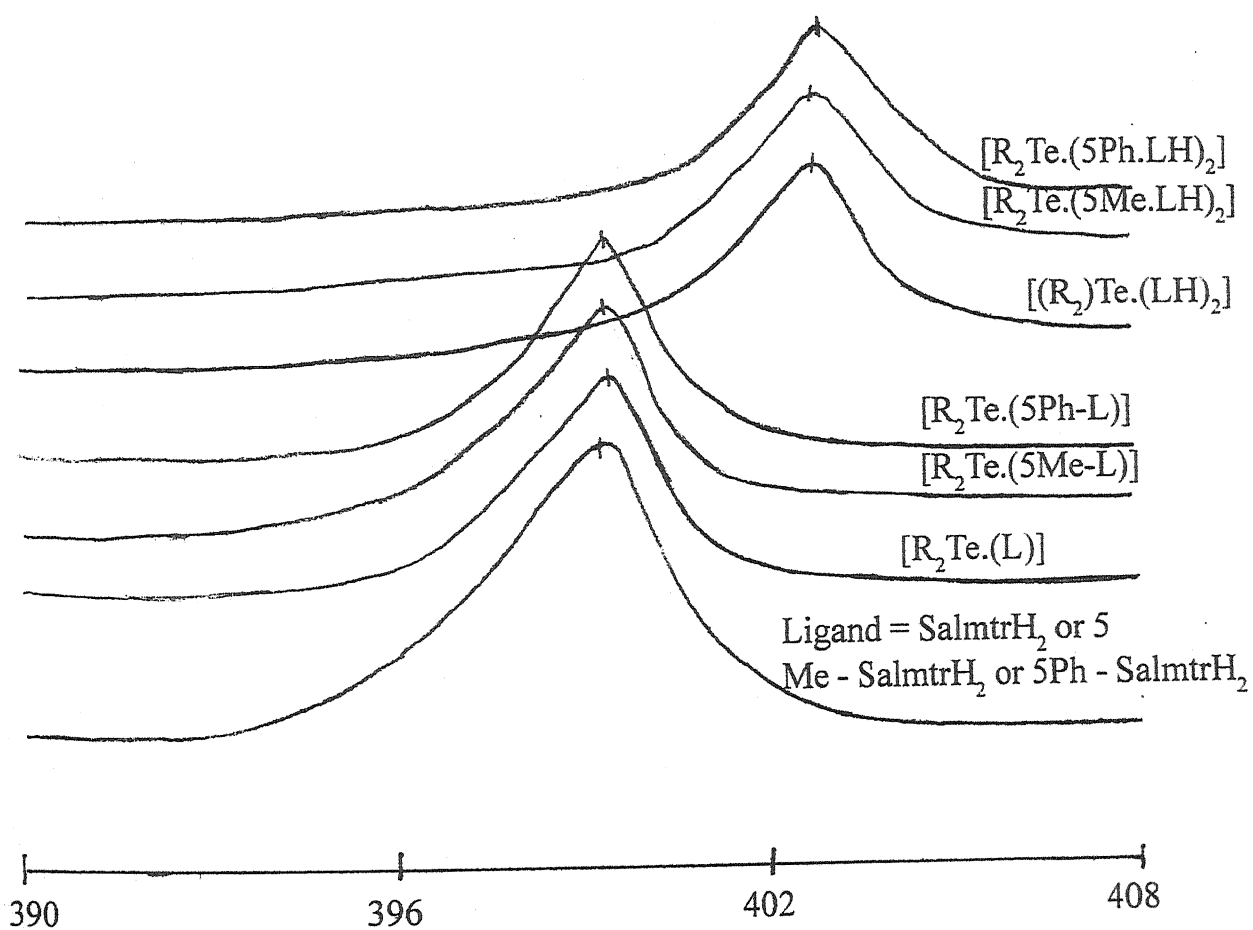


Fig 8 : N1s photoelectron peak in ligands, $[R_2Te.(L)]$ and $[(R_2)Te.(LH)_2]$ complexes

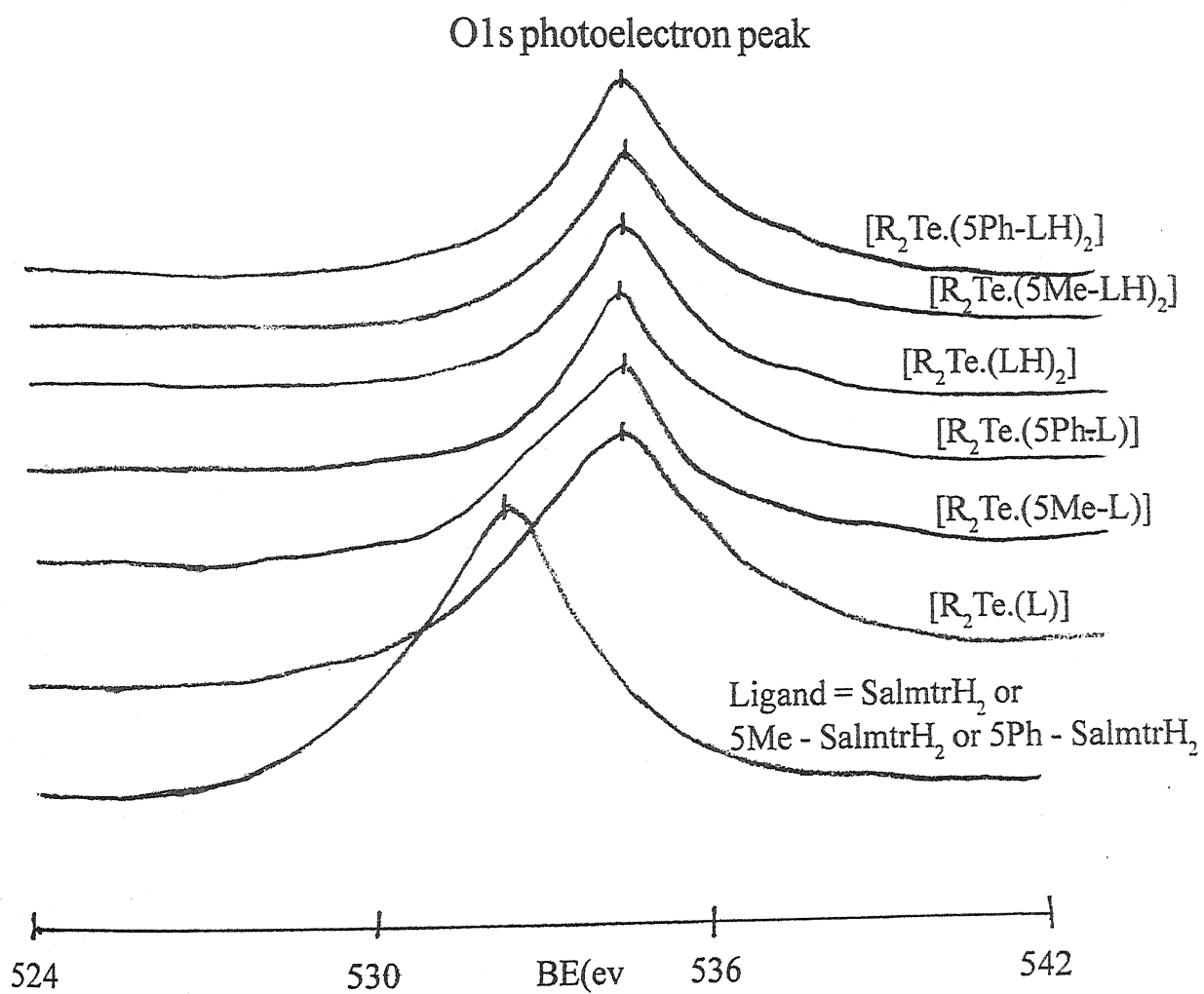


Fig 9 : O1s binding energies in Ligands $[R_2Te.(L)]$ and $[R_2Te.(LH)_2]$

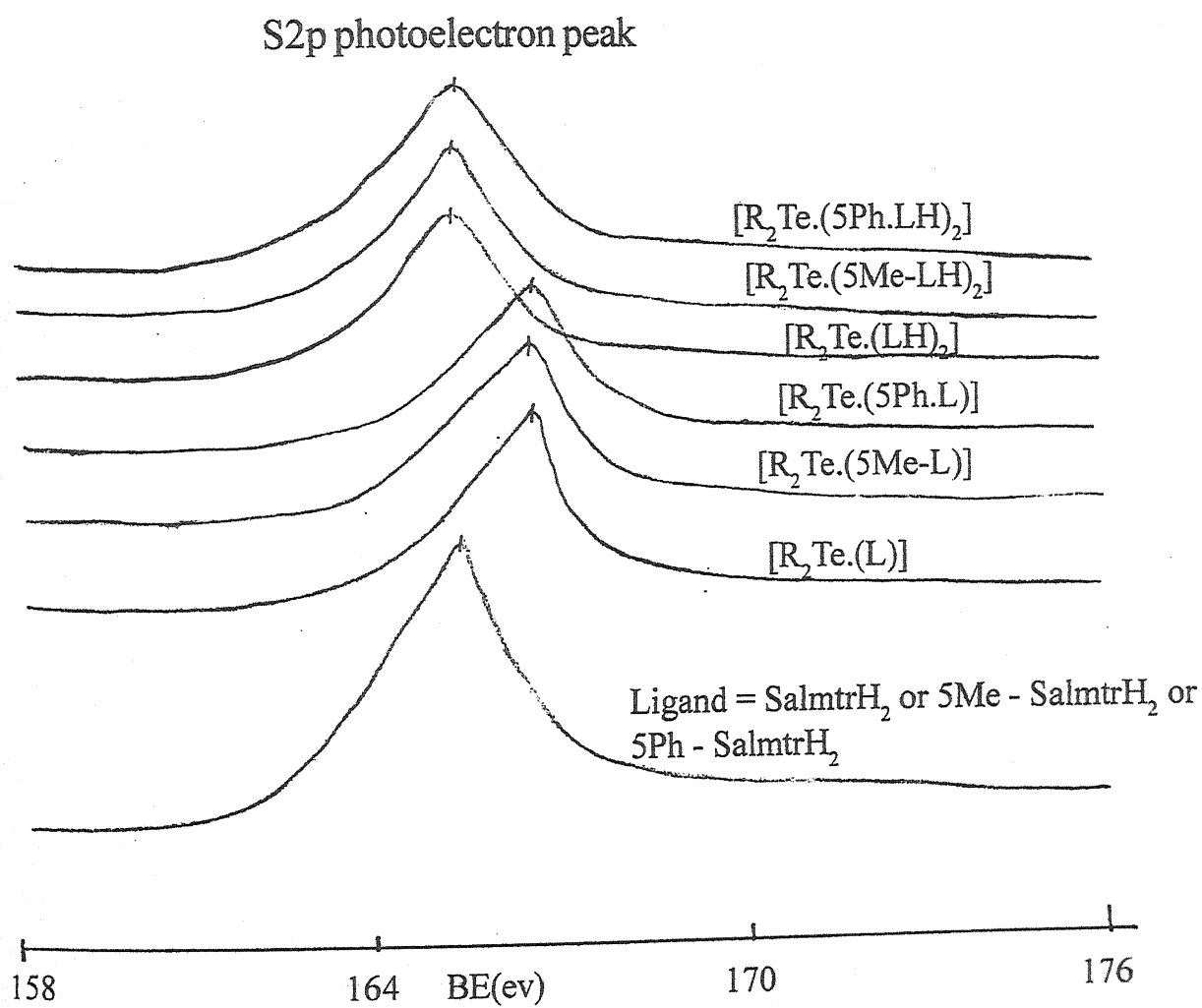


Fig 10 : S2p binding energies (ev) in Ligands; $[R_2Te.(L)]$ and $[R_2Te.(LH)_2]$ complexes

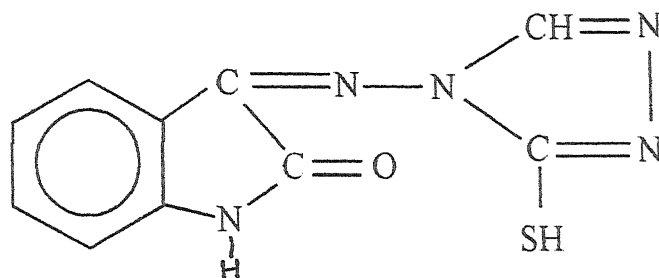
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CHAPTER IV
COMPLEXES OF
 R_2TeX_2 WITH 3-
MERCAPTO-4- β -
ISATINYLIMINO-1,2,4-
TRIAZOLE

"COMPLEXES OF R_2TeX_2 WITH 3-MERCAPTO-4- β -ISATINYLIMINO-1,2,4-TRIAZOLE"

4-amino-3-mercapto-1,2,4-triazole(mtrH) readily condenses with isatine in hot methanol giving 3-mercapto-4- β -isatinylimino-1,2,4-triazole(IstmtrH).



Structure of (Ist mtrH)

The considered Schiff Base (IstmtrH) contains several donor sites, four nitro, one sulphur and one oxygen.

EXPERIMENTAL

Preparation of $[R_2TeX_2(IstmtrH)]$

The R_2TeX_2 (1mmol) i.e. $(C_6H_5CH_2)_2TeI_2$; $(C_6H_4)_2TeCl_2$; $(p-MeOC_6H_4)_2TeCl_2$; $(p-Me_2N.C_6H_4)PhTeCl_2$; $(p-Me_2NC_6H_4)(p-MeOC_6H_4)TeCl_2$; $[(p-Me_2NC_6H_4)(p-EtOC_6H_4)TeCl_2]$ and $(CH_3)_2TeI_2$ was dissolved in CH_3OH with istmtrH ligand (1 mmol) and refluxed for 2-3 hrs. The solid product obtained after rotary evaporation was purified by pet. Ether(b.p. 60-80°), air-dried and kept in desiccators.

Preparation of $[R_2Te(Istmtr)_2]$

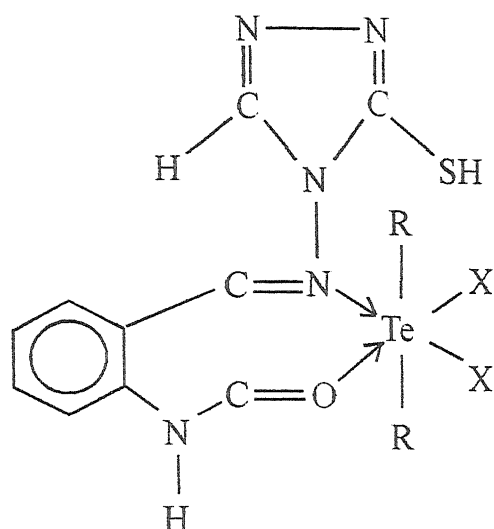
The R_2TeX_2 (1mmol) i.e. $(C_6H_5CH_2)_2TeI_2$; $(C_6H_4)_2TeCl_2$; $(p-MeOC_6H_4)_2TeCl_2$; $(p-Me_2N.C_6H_4)PhTeCl_2$; $(p-Me_2NC_6H_4)(p-MeOC_6H_4)TeCl_2$; $[(p-Me_2NC_6H_4)(p-EtOC_6H_4)TeCl_2]$ and $(CH_3)_2TeI_2$ was dissolved in CH_3OH with istmtrH ligand (2 mmol) and refluxed for 3 hrs. The solid product obtained after rotary evaporation was purified by pet. Ether(b.p. 60-80°), air-dried and kept in desiccators.

Results and Discussions

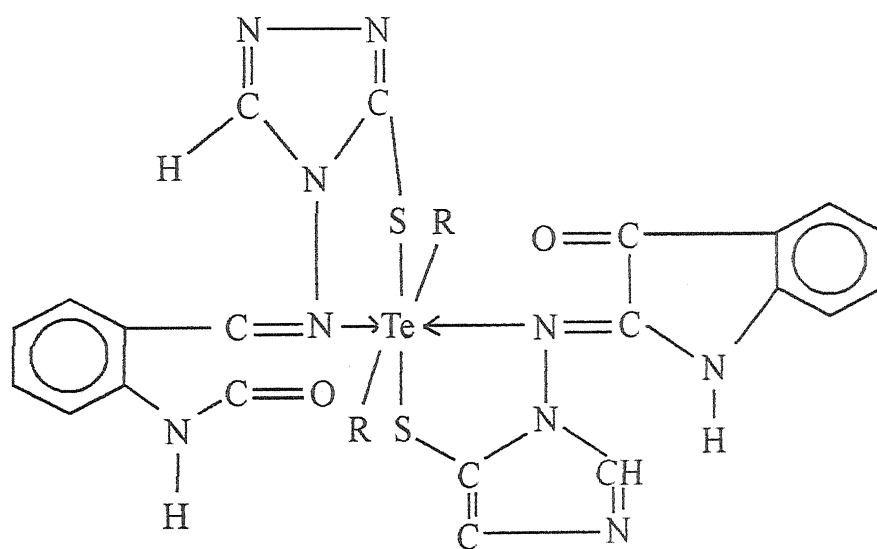
The results of elemental analysis and molar conductivity of $[R_2TeX_2.(IstmtrH)]$ and $[R_2Te.(Istmtr)_2]$ complexes are listed in table 1. The complexes are quite stable in air and partially soluble in methanol, ethanol, dioxin, DMF and DMSO. The DMF solutions of complexes at room temperature display negligible electrical conductance value indicating their non-ionic nature¹.

IR data of ligand (IstmtrH) are listed in table 2. The prepared $[R_2TeX_2.(IstmtrH)]$ complexes and $[R_2TeX_2.(Istmtr)_2]$ complexes exhibited $\nu_{C=N}$ band at around 1620 – 1610 cm^{-1} . The lowering of this band in the complexes indicates the coordination of nitrogen atoms of azomethine groups to the tellurium metal ion the far IR for $Te-N^2$ and ν_{Te-C^2} appeared at 420-410, and 560-540 cm^{-1} respectively. But ν_{Te-X} were absent in $[R_2Te(Istmtr)_2]$ complexes. The $\nu_{C=O}$ band (isatinic ketone) in $[R_2TeX_2.(IstmtrH)]$ complexes at 1720-1740, which normally appeared in ligand at 1760-1732 cm^{-1} . The lowering of $\nu_{C=O}$ in the complexes also indicate the coordination of oxygen atom of isatinic ketone with tellurium metal ion. But the position of $\nu_{C=O}$ in $[R_2Te(Istmtr)_2]$ complexes does not change with respect of ligand. This indicate the non-coordination of oxygen of isatinic ketone with tellurium metal ion in these complexes. The thioamide band I, and II and III were observed in the ligand at 1498 cm^{-1} , 1375 and 1208 cm^{-1} , which is observed to appear on the same position in these $[R_2TeX_2.(IstmtrH)]$ tellurium metal complexes, suggesting non-involvement of thioamide group. But the frequency position of thioamide band I, II and III is observed to raised to higher frequencies in $[R_2Te(Istmtr)_2]$ complexes which are taken to be taken characteristic of coordinated thioamide group.

It was observed that the binding energy for $Te3d_{3/2, 5/2}$ in the starting material R_2TeX_2 was higher than their prepared complexes table 3. This observation concludes that electron density on Te metal ion has been increased by coordination of Schiff base ligands with tellurium metal ion³. (Fig. 1 & 2)



Structure of $[R_2TeX_2(IstmtrH)]$ complexes



Structure of $[R_2Te(Istmtr)_2]$ complexes

It was observed that N1s binding energies of C=N group were higher in all these prepared complexes than the ligands; suggesting involvement of nitrogen atom in the coordination. It was noticed that O1s binding energy in $[R_2TeX_2(IstmtrH)]$ complexes were higher than O1s binding energy of ligand suggesting involvement of oxygen atom in coordination but O1s binding

energy were same in the ligand and $[R_2Te(Istmtr)_2]$ complexes, suggesting non-involvement of oxygen atom in coordination in $[R_2Te(Istmtr)_2]$ complexes³ Fig.3 and 4. Moreover, $S2p_{3/2}$ photoelectron peak have shown same binding energy data in $[R_2TeX_2(IstmtrH)]$ complexes as in ligand suggesting non involvement of sulphur atom in coordination in these $[R_2Te(Istmtr)_2]$ complexes³ but in $[R_2Te(Istmtr)_2]$ complexes photoelectron binding energy is increased than the ligand, suggesting involvement of sulphur atom in coordination in these complexes i.e. in $[R_2Te(Istmtr)_2]$ complexes³ Fig5 and 6.

On the basis of elemental analysis, conductivity results showing the all the complexes to be non-ionic and IR and X-Ray photoelectron(XPS) identifying the site of coordination it is possible to conclude that all these prepared complexes have pseudooctahedral geometry as show in fig 7(a) and 7(b).

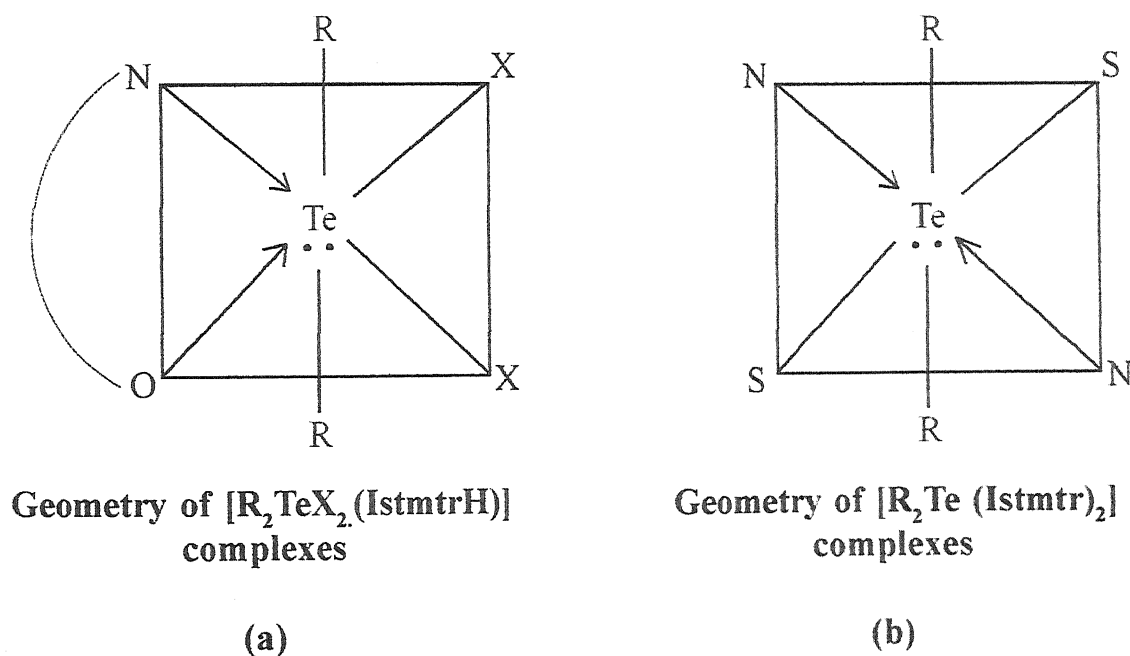


Fig. 7

Table 1:- Elemental analysis and molar conductivity values for the compounds

Sr. No	Compound	Found (Calc.)(%)				Molar conductivity (ohm-1 cm ² mol ⁻¹)
		Te	C	H	N	
1.	[(C ₆ H ₅ CH ₂) ₂ TeI ₂ .(IstmtrH)]	12.2 (12.0)	27.0 (27.1)	1.8 (1.9)	6.4 (6.6)	10
2.	[(C ₆ H ₄) ₂ TeCl ₂ .(IstmtrH)]	44.2 (44.3)	21.2 (21.4)	2.4 (2.5)	28.4 (28.5)	15
3.	[<i>p</i> -MeOC ₆ H ₄) ₂ TeCl ₂ .(IstmtrH)]	19.4 (19.8)	44.6 (44.8)	3.0 (3.2)	10.8 (10.9)	20
4.	[<i>p</i> -Me ₂ NC ₆ H ₄) ₂ PhTeCl ₂ .(IstmtrH)]	14.2 (14.4)	32.4 (32.5)	2.4 (2.5)	9.4 (9.5)	22
5.	[<i>p</i> -Me ₂ NC ₆ H ₄)(<i>p</i> -MeOC ₆ H ₄)TeCl ₂ .(IstmtrH)]	18.8 (18.9)	45.0 (45.2)	3.4 (3.5)	12.0 (12.4)	24
6.	[<i>p</i> -Me ₂ NC ₆ H ₄)(<i>p</i> -EtOC ₆ H ₄)TeCl ₂ .(IstmtrH)]	18.4 (18.6)	45.2 (45.6)	2.0 (2.3)	12.0 (12.2)	26
7.	(CH ₃) ₂ TeI ₂ (IstmtrH)]	0.1 (0.1)	15.4 (15.8)	1.4 (1.4)	7.6 (7.7)	28

Continue of Table 1

8.	$[(C_6H_5CH_2)_2Te.(Ismtr)_2]$	15.8 (15.9)	51.2 (51.4)	3.2 (3.3)	17.4 (17.5)	26
9.	$[(C_6H_4)_2Te.(Ismtr)_2]$	16.8 (16.6)	50.2 (50.0)	2.4 (2.6)	18.0 (18.2)	24
10.	$[p-MeOC_6H_4)_2Te(Ismtr)_2]$	15.4 (15.6)	50.5 (50.8)	3.0 (3.1)	17.0 (17.2)	22
11.	$[p-Me_2NC_6H_4)_2Ph Te.(Ismtr)_2]$	15.4 (15.7)	50.0 (50.2)	3.3 (3.3)	18.8 (18.9)	20
12.	$[p-Me_2NC_6H_4)(p-MeOC_6H_4)_2 Te.(Ismtr)_2]$	15.0 (15.1)	49.6 (49.8)	3.2 (3.4)	18.2 (18.3)	26
13.	$[p-Me_2NC_6H_4)(p-EtOC_6H_4)_2 Te.(Ismtr)_2]$	14.8 (14.9)	50.2 (50.4)	3.4 (3.6)	17.8 (17.9)	22
14.	$[(CH_3)_2Te.(Ismtr)_2]$	19.6 (19.8)	40.6 (40.8)	2.6 (2.8)	21.6 (21.7)	14

Table 2:- IR of Ligand (IstmtrH)

Band Position	Assignments
3220-3100 abr	NH stretching band
2950 wbr	C-H stretching band
2840-2800 wbr	
1820 wbr	Over tone band
1760 wbr	V _{C=O} isatonic ketone
1732 vsbr	
1655-1632 vsbr	Azomethyl (C=N)+ V _{C=C}
1498 s	Thioamide band I
1440 sbr	Phenyl ring skeletal band
1375 mbr	Thioamide band II
1350 W	δ NH
1325 wbr	V _{C-N} of triazole + V _{C-N} of side chain

Continue of Table 2

1270 s	
1240 wbr	
1208 s	Thioamide band III
1170 wbr	Phenyl and triazole
1105 m	Ring different mode of vibrations
1062 mbr	
1015 mbr	
970 m	
945 m	Thioamide band IV
852 mbr	C-H and N-H out of plane bending band.
760-755 sbr	
705	
660 mbr	Triazole and isatine part ring deformation vibrations.

Continue of Table 2

615-600 mbr	
560 wbr	
362 wbr	

W = weak, wbr = weak and board, m= medium, mbr = medium and board; s = strong, sbr = strong and broad, vsbr = very strong and broad

Table 3:- $Te3d_{3/2, 5/2}$, $N1s$, $O1s$ and $S2p$ binding energies (ev) in ligand (IstmtrH), $[R_2TeX_2(IstmtrH)]$ and $[R_2Te(Istmtr)_2]$ complexes

Sr. No.	Compound	Metal Ion		N1s(for ligand nitrogen only)	O1s for ligand Oxygen	S2p
		$Te3d_{3/2}$	$Te3d_{5/2}$			
1.	Ligand(IstmtrH)	-	-	400.2	533.2	165.2
2.	$(C_6H_5CH_2)_2TeI_2$	585.8	575.4	-	-	-
3.	$[(C_6H_5CH_2)_2TeI_2(IstmtrH)]$	584.0	574.0	402.8	534.8	165.2
4.	$[(C_6H_5CH_2)_2Te(Istmtr)_2]$	584.0	574.0	402.8	532.2	166.0
5.	$(C_6H_4)_2TeCl_2$	585.6	575.2	-	-	-
6.	$[(C_6H_4)_2TeCl_2(IstmtrH)]$	584.4	574.0	402.8	534.6	165.2
7.	$[(C_6H_5)_2Te(Istmtr)_2]$	584.4	574.0	402.8	533.2	166.0
8.	$[p-MeOC_6H_4)_2TeCl_2]$	585.8	575.4	-	-	-
9.	$[p-MeOC_6H_4)_2TeCl_2(IstmtrH)]$	584.6	574.2	402.6	534.6	165.2
10.	$[p-MeOC_6H_4)_2Te(Istmtr)_2]$	584.6	574.2	402.6	533.2	166.0
11.	$(p-MeNC_6H_4)PhTeCl_2$	585.6	575.6	-	-	-
12.	$[p-MeNC_6H_4)_2PhTeCl_2(IstmtrH)]$	584.2	574.2	402.6	534.8	165.2
13.	$[p-MeNC_6H_4)_2PhTe(Istmtr)_2]$	584.2	574.2	402.6	533.2	166.0
14.	$[p-MeNC_6H_4)(p-MeOC_6H_4)TeCl_2]$	585.8	575.4	-	-	-

Continue of Table 3

15.	$[(p\text{-MeNC}_6\text{H}_4)(p\text{-MeOC}_6\text{H}_4)\text{TeCl}_2(\text{IsmttrH})]$	584.4	574.2	402.6	534.8	165.2
16.	$[(p\text{-Me}_2\text{NC}_6\text{H}_4)(p\text{-MeOC}_6\text{H}_4)\text{Te}(\text{IsmttrH})_2]$	584.4	574.2	402.6	533.2	166.0
17.	$[(p\text{-MeNC}_6\text{H}_4)(p\text{-EtOC}_6\text{H}_4)\text{TeCl}_2]$	585.4	575.6	-	-	-
18.	$[(p\text{-MeNC}_6\text{H}_4)(p\text{-EtOC}_6\text{H}_4)\text{TeCl}_2(\text{IsmttrH})]$	584.2	584.2	402.8	534.8	165.2
19.	$[(p\text{-Me}_2\text{NC}_6\text{H}_4)(p\text{-EtOC}_6\text{H}_4)\text{Te}(\text{IsmttrH})_2]$	584.2	584.2	402.8	533.2	166.0
20.	$(\text{CH}_3)_2\text{TeI}_2$	585.6	575.8	-	-	-
21.	$(\text{CH}_3)_2\text{TeI}_2(\text{IsmttrH})]$	584.2	584.2	402.6	534.8	165.2
22.	$[(\text{CH}_3)_2\text{Te}(\text{IsmttrH})_2]$	584.2	584.2	402.6	533.2	166.0

Te3d_{3/2} photoelectron spectra.

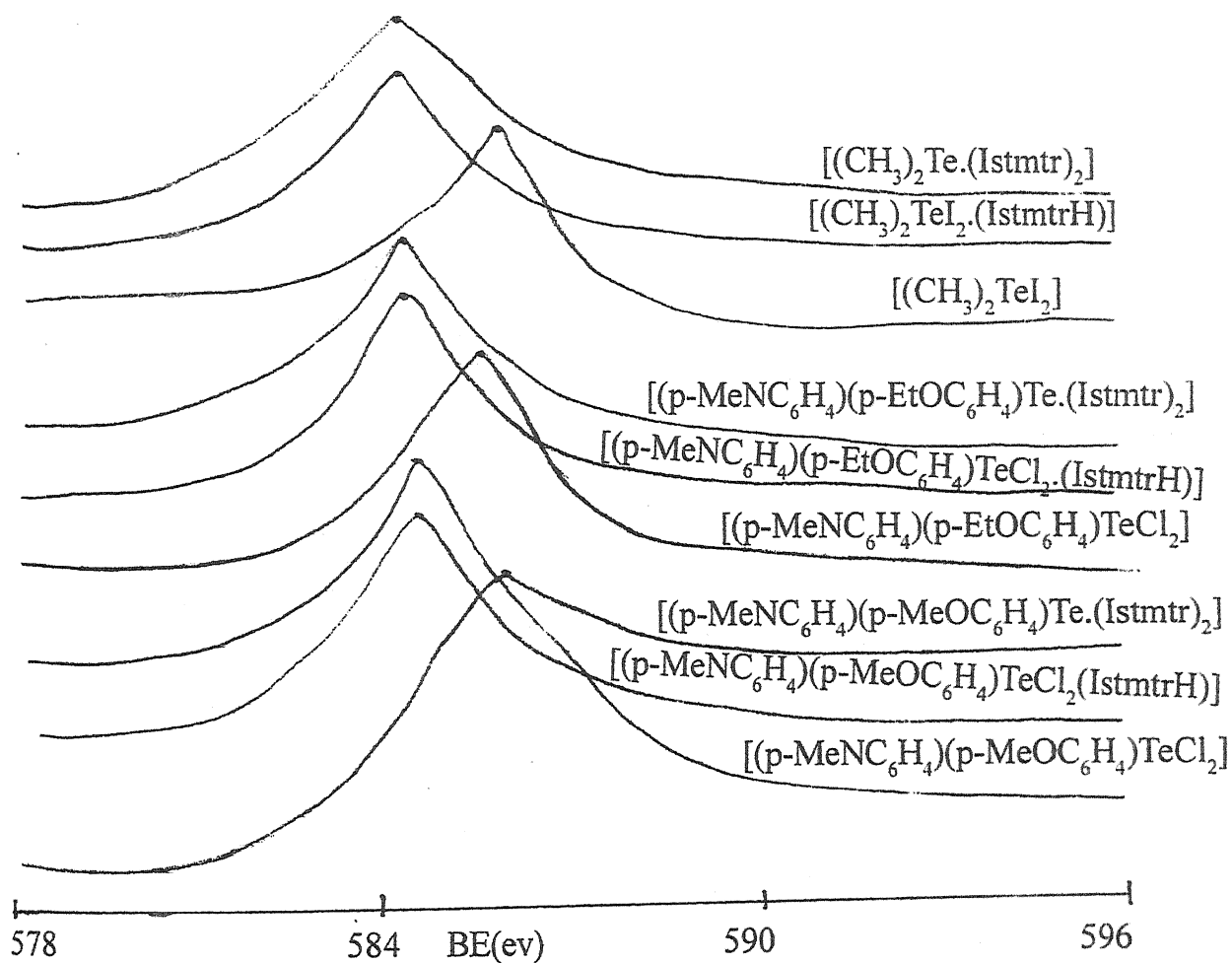


Fig 1 : Te 3d_{3/2} binding energies (ev) in [R₂TeX₂]; [R₂TeX₂(IstmtrH)] and [R₂Te.(Istmtr)₂] complexes

Te3d_{3/2} photoelectron peak.

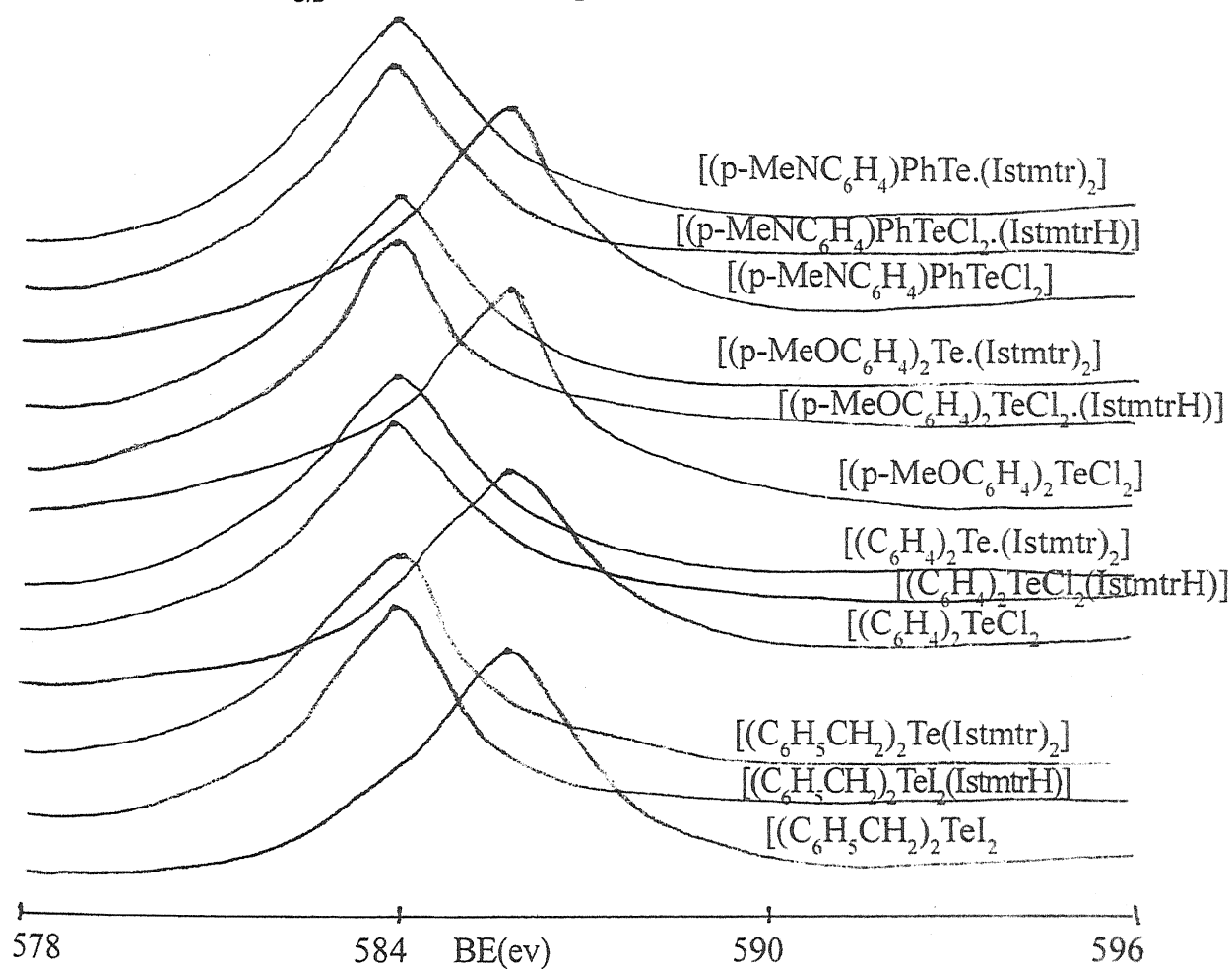


Fig 2 : Te 3d_{3/2} binding energies (ev) in $[\text{R}_2\text{TeX}_2]$; $[\text{R}_2\text{TeX}_2(\text{IstmtrH})]$ and $[\text{R}_2\text{Te}(\text{Istmtr})_2]$ complexes

N1s photoelectron spectra

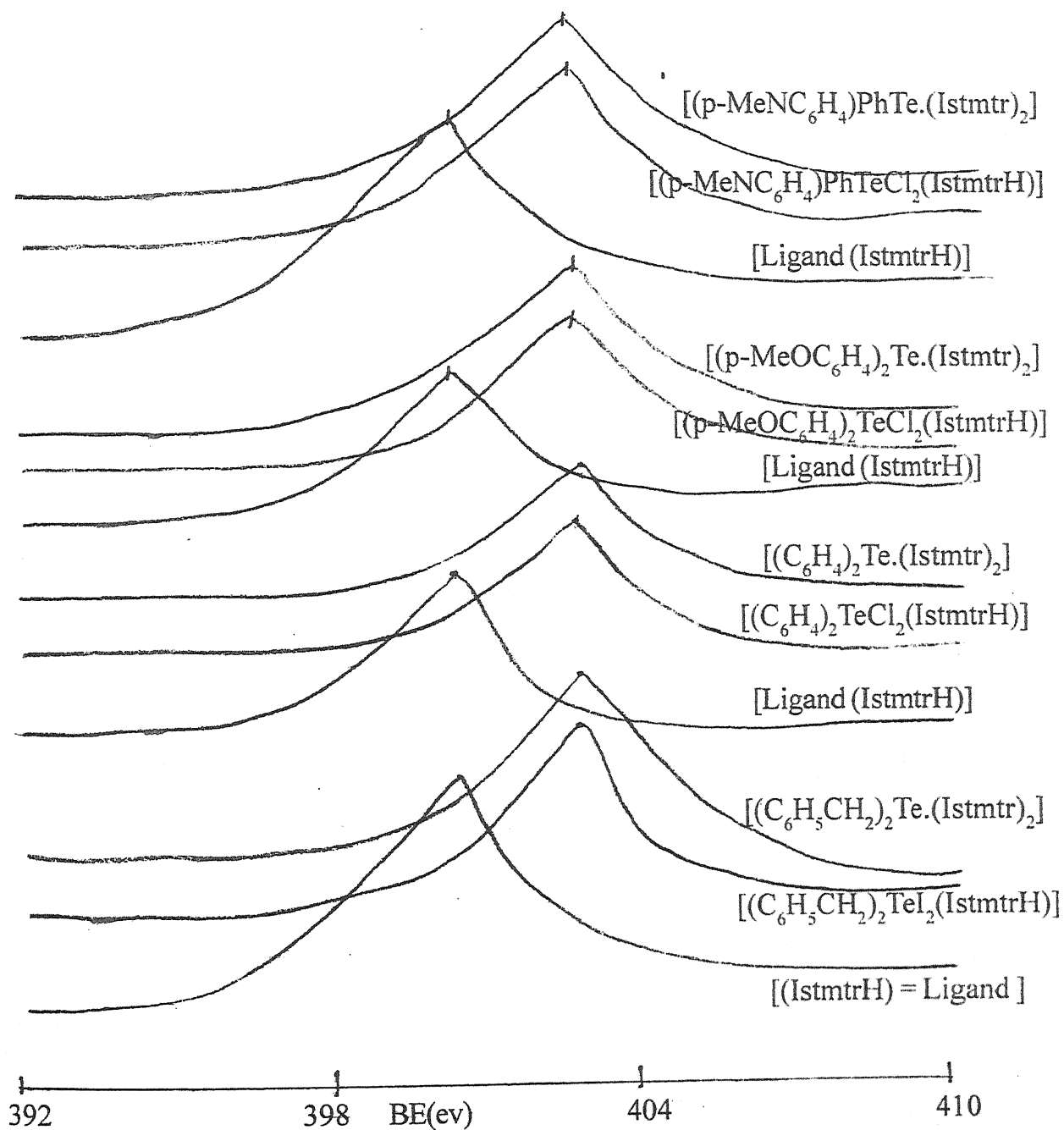


Fig 3 : N1s binding energies (ev) in (IstmtrH) Ligand, $[\text{R}_2\text{TeX}_2(\text{IstmtrH})]$ and $[\text{R}_2\text{Te}(\text{IstmtrH})_2]$ complexes

N1s photoelectron spectra

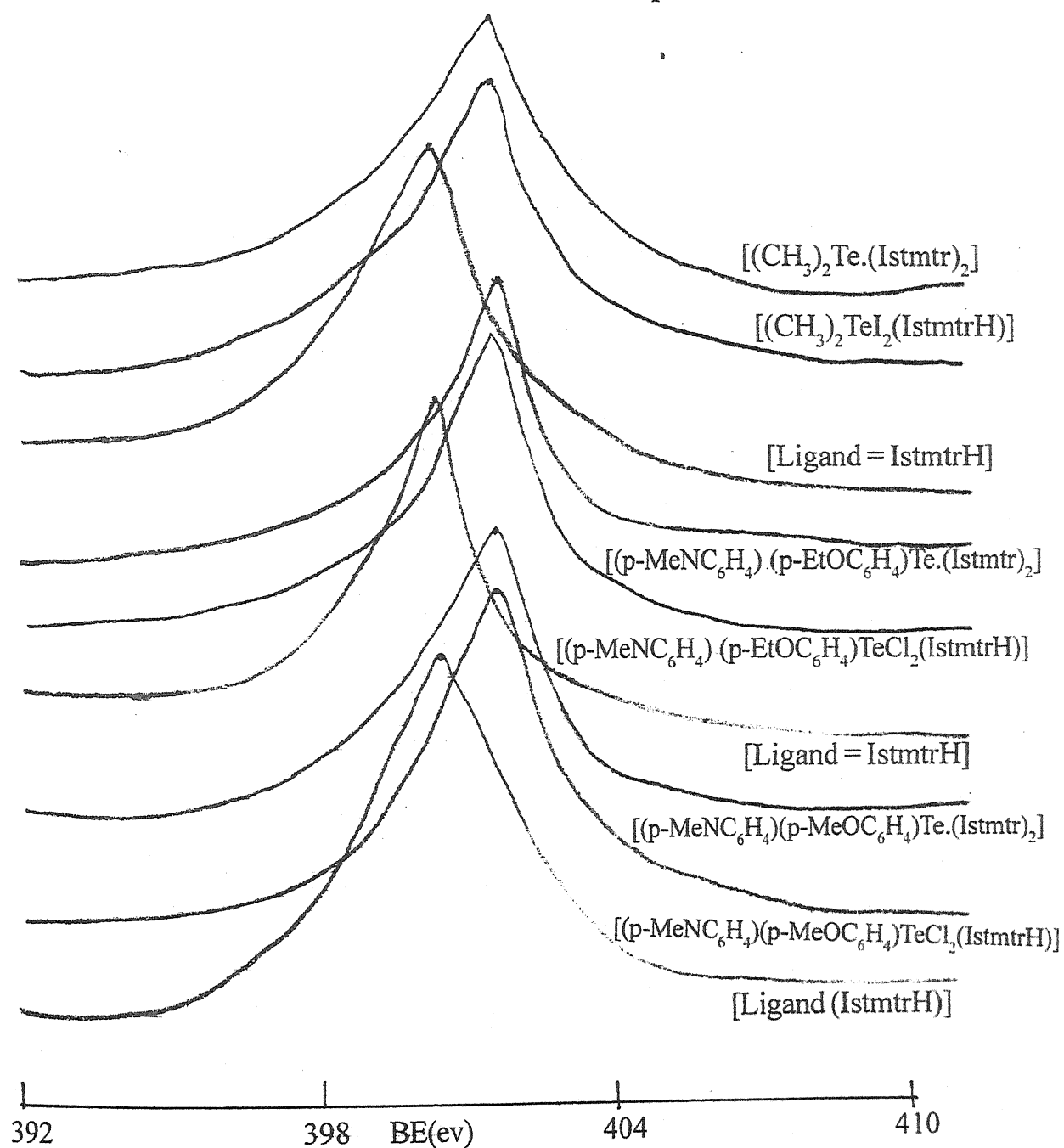


Fig 4 : N1s binding energies (ev) in (IstmtrH) Ligand, $[R_2TeX_2(IstmtrH)]$ and $[R_2Te.(Istmtr)_2]$ complexes

O1s photoelectron spectra

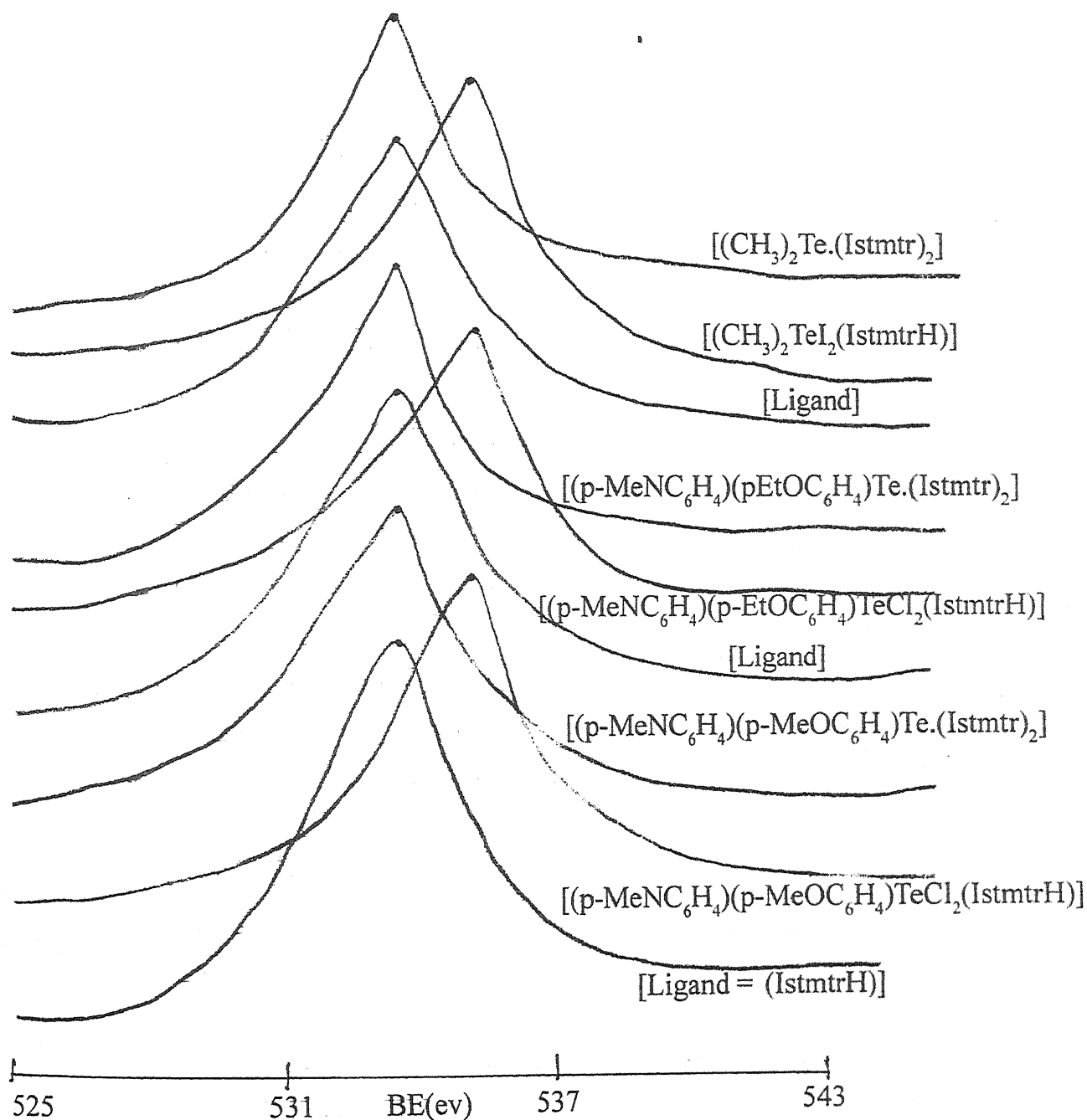


Fig 5 : O1s binding energies (ev) in Ligand, (IstmtrH) $[R_2TeX_2.(IstmtrH)]$ and $[R_2Te.(Istmtr)_2]$ complexes

O1s photoelectron peak

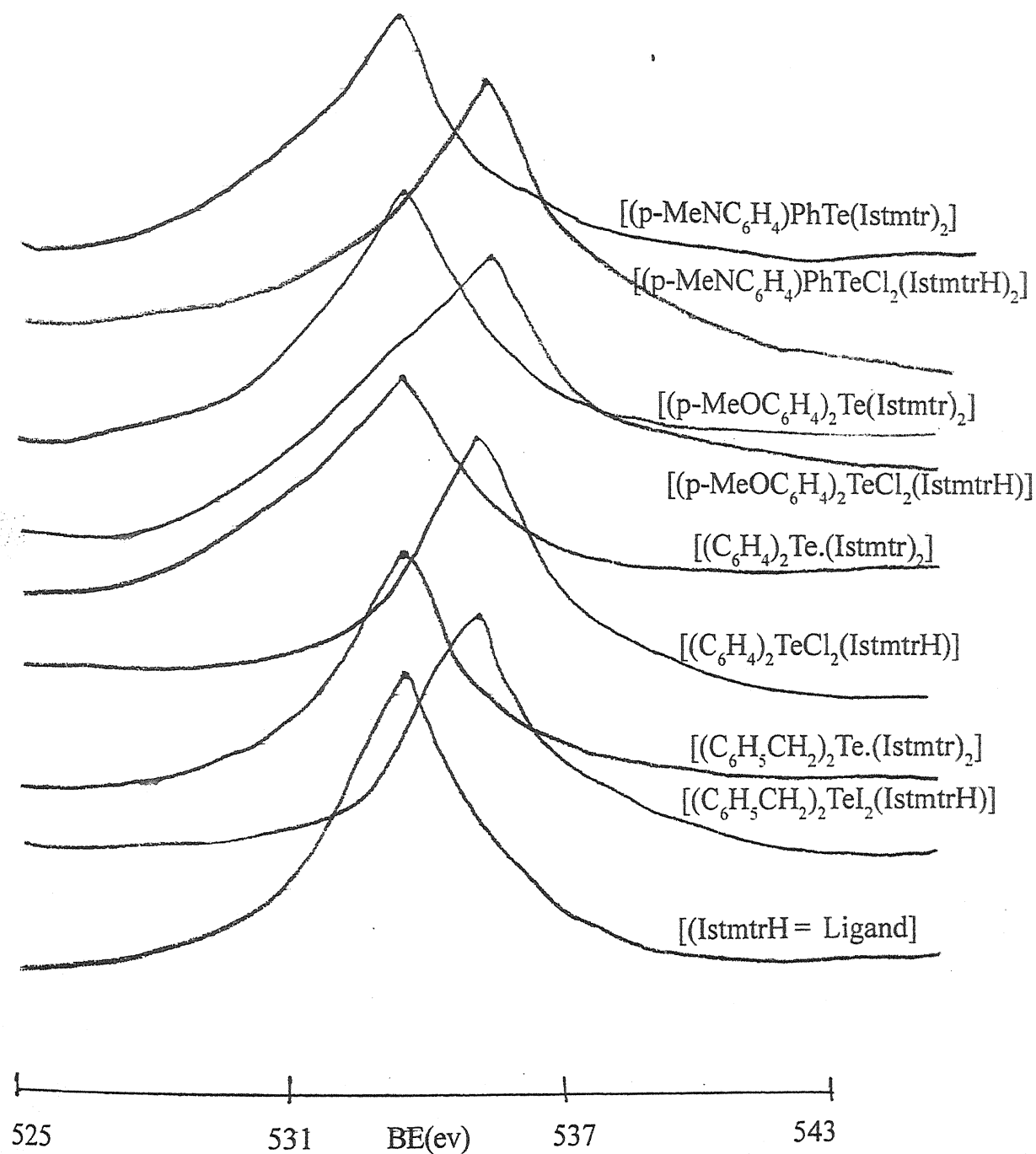


Fig 6 : O1s binding energies (ev) in Ligand, (IstmtrH), $[\text{R}_2\text{TeX}_2(\text{IstmtrH})]$ and $[\text{R}_2\text{Te}(\text{Istmtr})_2]$ complexes

S2p photoelectron spectra.

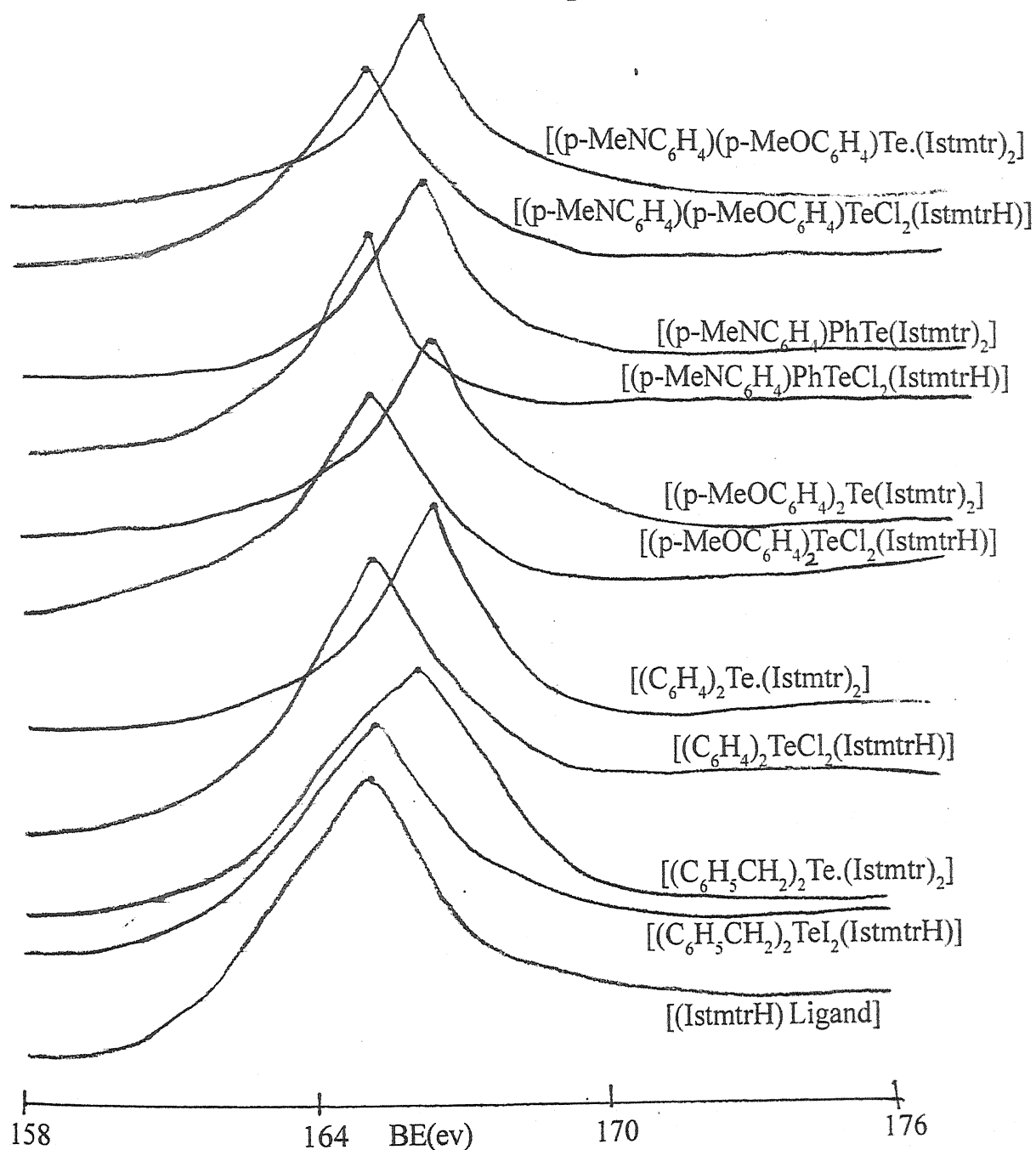


Fig 7(a) : S2p binding energies (ev) in Ligand, $[\text{R}_2\text{TeX}_2(\text{IstmtrH})]$ and $[\text{R}_2\text{Te}(\text{Istmtr})_2]$ complexes

S2p photoelectron Spectra.

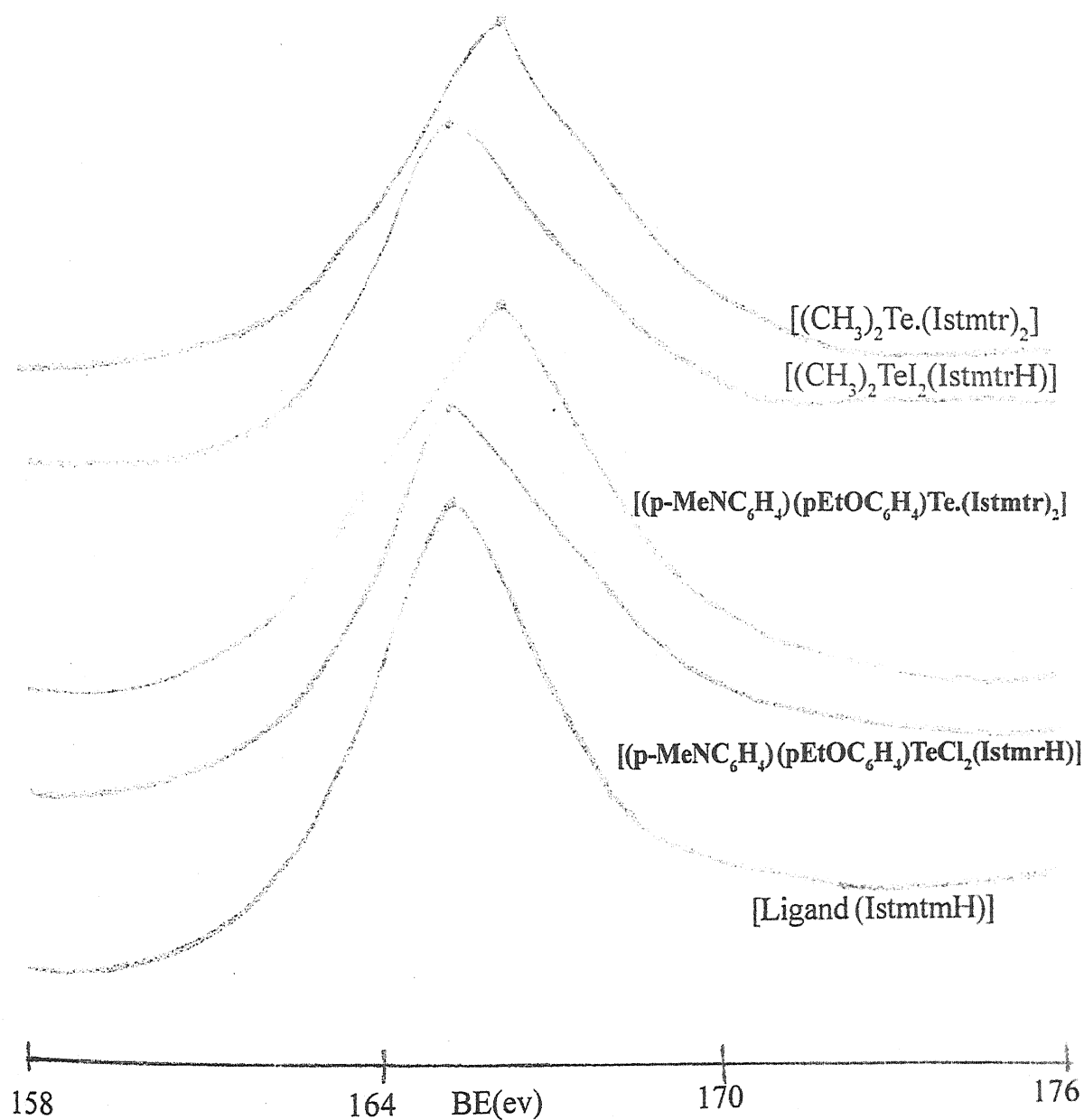


Fig 7(b) : S2p binding energies (ev) in ligand, $[\text{R}_2\text{TeX}_2(\text{IstmtrH})]$ and $[\text{R}_2\text{Te} \cdot (\text{Istmtr})_2]$ complexes

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1. W.J.Greary : Coord.chem.Rev. 7,81(1971)
2. Y.D. Kulkarni and S. Srivastava : Indian J.Chem., 24A, 710(1985)
3. S.Srivastava : Applied spectro Sc. Rev., 22,
401(1986)

Chapter - V

“COMPLEXES OF

R_2TeX_2 WITH

α - PHENYL -

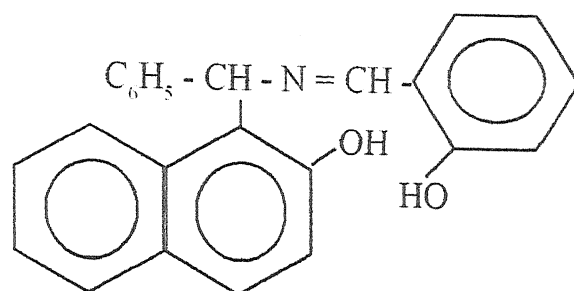
SALICYLALDIMINO

METHYL - β -

NAPTHOL”

"COMPLEXES OF R_2TeX_2 WITH α -PHENYL-SALICYLALDIMINO-METHYL- β -NAPTHOL"

The Schiff base, α -phenylsalicylaldiminomethyl- β -naphthol (i.e. $pSnH_2$) is potential tridentate (O,N,O) donor ligand and is expected to behave as monoanionic or dianionic coordinating molecular by deprotonation of one phenolic OH or both phenolic OH respectively.



α - phenylsalicylaldiminomethyl - β - naphthol (i.e. $psnH_2$)

Although many molecular adducts of R_2TeX_2 with various Schiff base ligands have been synthesized and characterized by various spectroscopy to establish their bonding, the interaction of R_2TeX_2 with ONO donor Schiff base ligands are scarce ¹. This chapters deal with the interaction of R_2TeX_2 with α -phenylsalicylaldimino methyl- β -naphthol (i.e. $pSnH_2$) and establish geometry of the products.

Preparation of $[R_2Te(psn)]$

The R_2TeX_2 (1mmol) i.e. $(C_6H_5CH_2)TeI_2$; $(C_6H_4)_2TeCl_2$; (*p*-MeOC₆H₄)TeCl₂; (*p*-Me₂N.CH₄)C₆H₅TeCl₂; (*p*-Me₂N.C₆H₄) (*p*-EtOC₆H₄)TeCl₂]; and $(CH_3)_2TeI_2$ was dissolved in 50 ml dry methanol and α -

phenyl Salicylaldimino methyl- β -naphthol i.e. ($p\text{SnH}_2$) (1mmol) was mixed in above solution drop by drop wise and mixture was refluxed for 3-4 hrs. The Resulting solid product was filtered washed with pet-ether and air-dried.

Preparation of $[R_2\text{Te}(\text{psnH})_2]$

The $R_2\text{TeX}_2$ (1mmol) i.e. $(\text{C}_6\text{H}_5\text{CH}_2)\text{TeI}_2$; $(\text{C}_6\text{H}_4)_2\text{TeCl}_2$; ($p\text{-MeOC}_6\text{H}_4$) $_2\text{TeCl}_2$; ($p\text{-Me}_2\text{N.C}_6\text{H}_4$) $\text{C}_6\text{H}_5\text{TeCl}_2$; ($p\text{-Me}_2\text{N.C}_6\text{H}_4$) ($p\text{-EtOC}_6\text{H}_4$) TeCl_2 ; and $(\text{CH}_3)_2\text{TeI}_2$ was dissolved in 50 ml dry methanol and α -phenyl Salicylaldimino methyl- β -naphthol i.e. ($p\text{SnH}_2$) (2mmol) was mixed in above solution. The mixture was refluxed for 3-4 hrs. and the resulting solid product was obtained, filtered. It washed with pet-ether and air-dried.

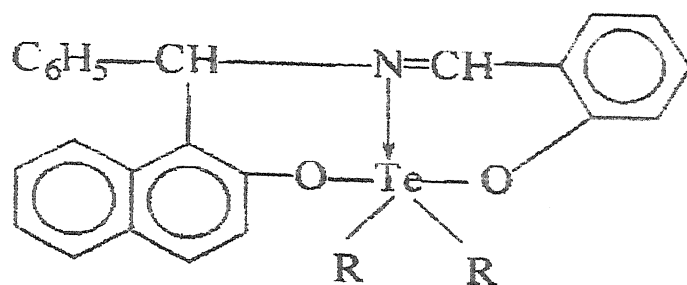
RESULT AND DISCUSSIONS

The all prepared complexes $[R_2\text{Te}(p\text{Sn})]$ and $[R_2\text{Te}(\text{psnH})_2]$ were found to be air stable. The molar conductance values of all the complexes in acetone were observed 20-30 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ indicating they are non electrolyte in nature².

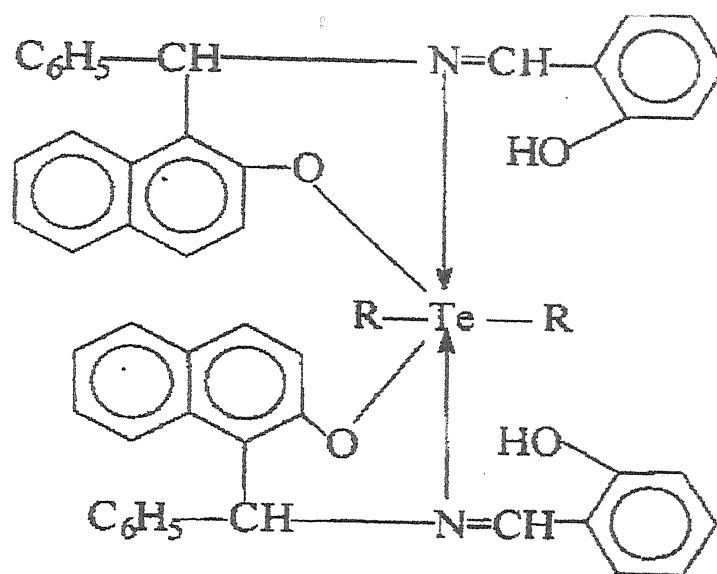
The free ligand displays a strong broad band at 3270-3220 cm^{-1} attributed from VOH of phenolic group of ligand. The VOH of ligand disappeared in these $[R_2\text{Te}(\text{psn})]$ complexes suggesting deprotonation of both penolic proton in the complexes. But in case of $[R_2\text{Te}(\text{psnH})_2]$. Its presence was observed.

The strong band at 1620 cm^{-1} in free ligand is attributed to $\nu_{\text{C=N}}$ which shifts to lower frequency in almost all the complexes suggesting coordination of aldimino $\nu(\text{C=N})$ nitrogen to metal ion. The far IR for $\nu_{\text{Te-N}}$, $\nu_{\text{Te-C}}$ were

appeared at 420-410 and 560-540 cm^{-1} in all these prepared complexes³, while $\nu_{\text{Te-Cl}}$ was found absent which normally appear at 270 - 300 cm^{-1} .



Structure of $[\text{R}_2\text{Te}(\text{psn})]$



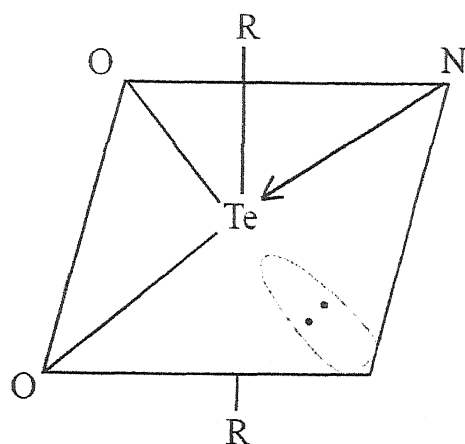
Structure of $[\text{R}_2\text{Te}(\text{psnH})_2]$

XPS data of $\text{Te}3d_{3/2, 5/2}$, $\text{N}1s$ and $\text{O}1s$ $[\text{R}_2\text{Te}(\text{psn})]$ and $[\text{R}_2\text{Te}(\text{psnH})_2]$ complexes are listed in table 2. It was observed that the binding energy of $\text{Te}3d_{3/2, 5/2}$ in the starting material was higher than their prepared molecular adducts. These observations concluded that electron density on tellurium metal ion has been increased by coordination of Schiff base ligands with tellurium metal ion. ⁴(Fig 1 and 2).

It was noticed that N1s binding of C=N group were higher in all these $[R_2Te(pSn)]$ and $[R_2Te(psnH)_2]$ complexes than ligands; suggesting involvement of nitrogen atom of (C=N group) in the complexation (Fig. 4 and 5). Furthermore, it was noticed O1s binding energy were more in $[R_2Te(psn)]$ and $[R_2Te(psnH)_2]$ complexes, than ligands suggesting the involvement of oxygen atom in the complexes⁴. In case of $[R_2Te(psnH)_2]$ complexes O1s photoelectron peak have shown two peaks with same intensity, one with same position as in ligand and other higher than ligand suggesting only two oxygen atoms are involved in coordination, remaining two oxygen atoms are uncoordinated⁴. (Fig. 5 and 6).

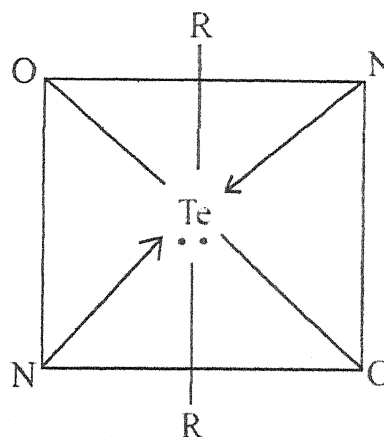
The X2p photoelectron spectra ($x = Cl$ or I) were observed absent in $[R_2Te(psnH)_2]$ complexes and $[R_2Te(psn)]$ complexes.

On the basis of elemental analysis, molar conductivity, IR and XPS data, it is possible to conclude that prepared molecular adducts $[R_2Te(psn)]$ have octahedral structure, while $[R_2Te(psnH)_2]$ molecular adducts are pseudo octahedral in geometry as shown in fig. 7(a) and fig. 7(b).



Geometry of $[R_2Te(psn)]$

(a)



Structure of $[R_2Te(psnH)_2]$

(b)

Fig. 7 : Geometry of $[R_2Te(psn)]$ and $[R_2Te(psnH)_2]$ complexes

Table 1: Elemental and molar conductivity of $[R_2Te(pSn)]$ and $[R_2Te(pSnH)_2]$ complexes

S.No.	Compound	Found (Calc.) (%)				Molar Conductivity (ohm ⁻¹ cm ² mol ⁻¹)
		Te	C	H	N	
1.	$[(C_6H_5CH_2)_2Te(pSn)]$	19.0 (19.3)	69.1 (69.0)	4.5 (4.7)	2.0 (2.1)	10
2.	$[(C_6H_4)_2Te.(pSn)]$	20.2 (20.0)	68.2 (68.7)	3.4 (3.9)	2.0 (2.2)	15
3.	$[(p-MeOC_6H_4)_2Te(pSn)]$	19.2 (19.3)	69.2 (69.0)	4.5 (4.6)	2.0 (2.1)	22
4.	$[(p-Me_2NC_6H_4)C_6H_5Te.(pSn)]$	16.2 (16.0)	69.2 (69.4)	5.2 (5.3)	5.2 (5.3)	24
5.	$[(p-Me_2NC_6H_4)(p-MeOC_6H_4)Te.(pSn)]$	18.2 (18.0)	66.2 (66.3)	4.6 (4.8)	3.8 (3.9)	28
6.	$[(p-Me_2NC_6H_4)(p-EtOC_6H_4)Te.(pSn)]$	17.2 (17.3)	65.0 (65.1)	5.0 (5.0)	3.6 (3.8)	18
7.	$[(CH_3)_2Te.(pSn)]$	24.6 (24.8)	2.6 (2.7)	4.2 (4.5)	6.0 (6.2)	16
8.	$[(C_6H_5CH_2)_2Te.(pSnH)_2]$	12.4 (12.6)	73.4 (73.5)	4.6 (4.7)	2.6 (2.7)	12
9.	$[(C_6H_4)_2Te.(pSnH)_2]$	12.8 (12.9)	73.2 (73.3)	4.2 (4.0)	2.8 (2.9)	14
10.	$[(p-MeOC_6H_4)_2Te(pSnH)_2]$	12.0 (12.2)	71.0 (71.2)	4.5 (4.6)	2.6 (2.7)	16
11.	$[(p-Me_2NC_6H_4)C_6H_5Te(pSnH)_2]$	12.2 (12.4)	72.4 (72.5)	4.6 (4.8)	4.2 (4.0)	12
12.	$[(p-Me_2NC_6H_4)(p-MeOC_6H_4)Te.(pSnH)_2]$	12.2 (12.4)	71.3 (71.6)	4.6 (4.7)	4.0 (4.0)	18
13.	$[(p-Me_2NC_6H_4)(p-EtOC_6H_4)Te.(pSn)]$	12.2 (12.0)	72.6 (72.8)	5.2 (5.0)	3.4 (3.9)	20
14.	$[(CH_3)_2Te.(pSnH)_2]$	14.6 (14.8)	69.6 (69.7)	4.2 (4.6)	3.0 (3.2)	22

Table 2:- $Te3d_{3/2,5/2}$ N1s and O1s binding energies (ev) in $(IstmtrH), [R_2TeX_2.(pSn)]$ and $[R_2Te.(pSnH)_2]$ complexes

S.No.	compounds	Metal $Te3d_{3/2}$	Ion $Te3d_{5/2}$	O1s	N1s
1.	Ligand($psnH$) ₂	-	-	532.6	399.0
2.	$(C_6H_5CH_2)_2TeI_2$	585.8	575.4	-	-
3.	$[(C_6H_5CH_2)_2Te(pSn)]$	584.2	574.0	534.4	400.8
4.	$[(C_6H_5CH_2)_2Te(pSnH)_2]$	584.2	574.0	532.6-534.4	400.8
5.	$(C_6H_4)_2TeCl_2$	585.6	575.2	-	-
6.	$[(C_6H_4)_2Te(pSn)]$	584.2	574.0	534.4	400.8
7.	$[(C_6H_4)_2Te(pSnH)_2]$	584.2	574.0	532.6-534.4	400.8
8.	$[(p-MeOC_6H_4)_2TeCl_2]$	585.8	575.4	-	-
9.	$[(p-MeOC_6H_4)_2Te(psn)]$	584.2	574.0	534.4	400.8
10.	$[(p-MeOC_6H_4)_2Te(psnH)_2]$	584.2	574.0	532.6-534.4	400.8
11.	$[(p-Me_2NC_6H_4) C_6H_5TeCl_2]$	585.6	575.6	-	-
12.	$[(p-Me_2NC_6H_4C_6H_5Te(psn)]$	584.0	574.2	534.4	400.8
13.	$[(p-Me_2NC_6H_4)_2 C_6H_5Te(psnH)_2]$	584.0	574.2	532.6-534.4	400.8
14.	$[(p-Me_2NC_6H_4) (p-MeOC_6H_4)TeCl_2]$	585.8	575.4	-	-
15.	$[(p-Me_2NC_6H_4) (p-MeOC_6H_4)Te.(psn)]$	584.0	574.2	534.6	400.8
16.	$[(p-Me_2NC_6H_4) (p-MeOC_6H_4)Te.(psnH)_2]$	584.0	574.2	532.6-534.6	400.8
17.	$[(p-Me_2NC_6H_4) (p-EtOC_6H_4)TeCl_2]$	585.4	575.6	-	-
18.	$[(p-Me_2NC_6H_4) (p-EtOC_6H_4)Te (psn)]$	584.0	574.2	534.6	400.8
19.	$[p-Me_2NC_6H_4 (p-EtOC_6H_4)Te(psnH)_2]$	584.0	574.2	532.6-534.6	400.8
20.	$[(CH_3)_2 TeI_2]$	585.6	575.8	-	-
21.	$[(CH_3)_2 Te(psn)]$	584.0	574.2	534.6	400.8
22.	$[(CH_3)_2 Te(psnH)_2]$	584.0	574.2	532.6-534.6	400.8

Te3d_{3/2} photoelectron peak.

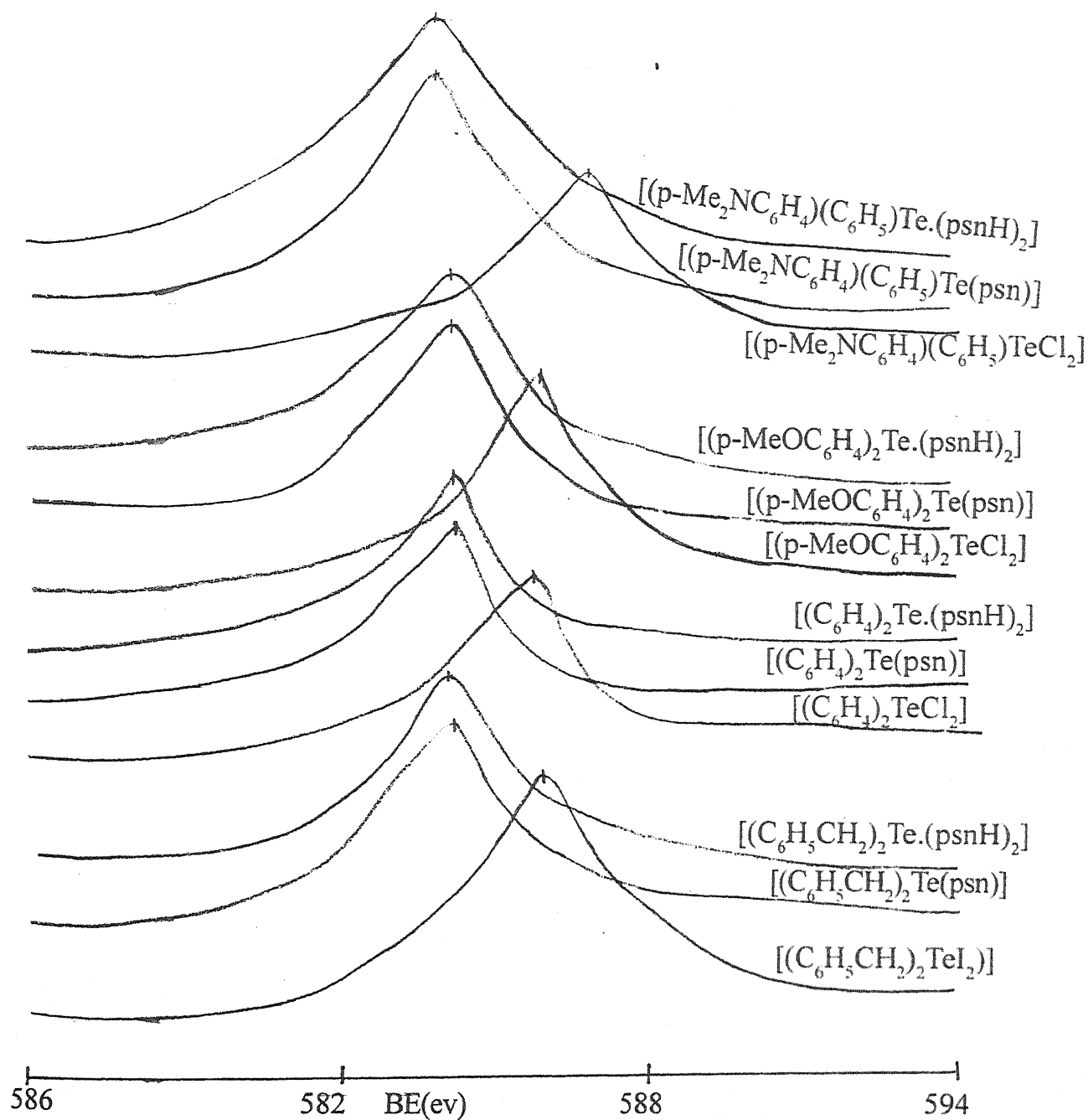


Fig 1 : Te 3d_{3/2} binding energies (ev) in $[\text{R}_2\text{TeX}_2]$; $[\text{R}_2\text{Te}(\text{psn})]$ and $[\text{R}_2\text{Te}(\text{psnH})_2]$ complexes

Te3d_{3/2} photoelectron peak.

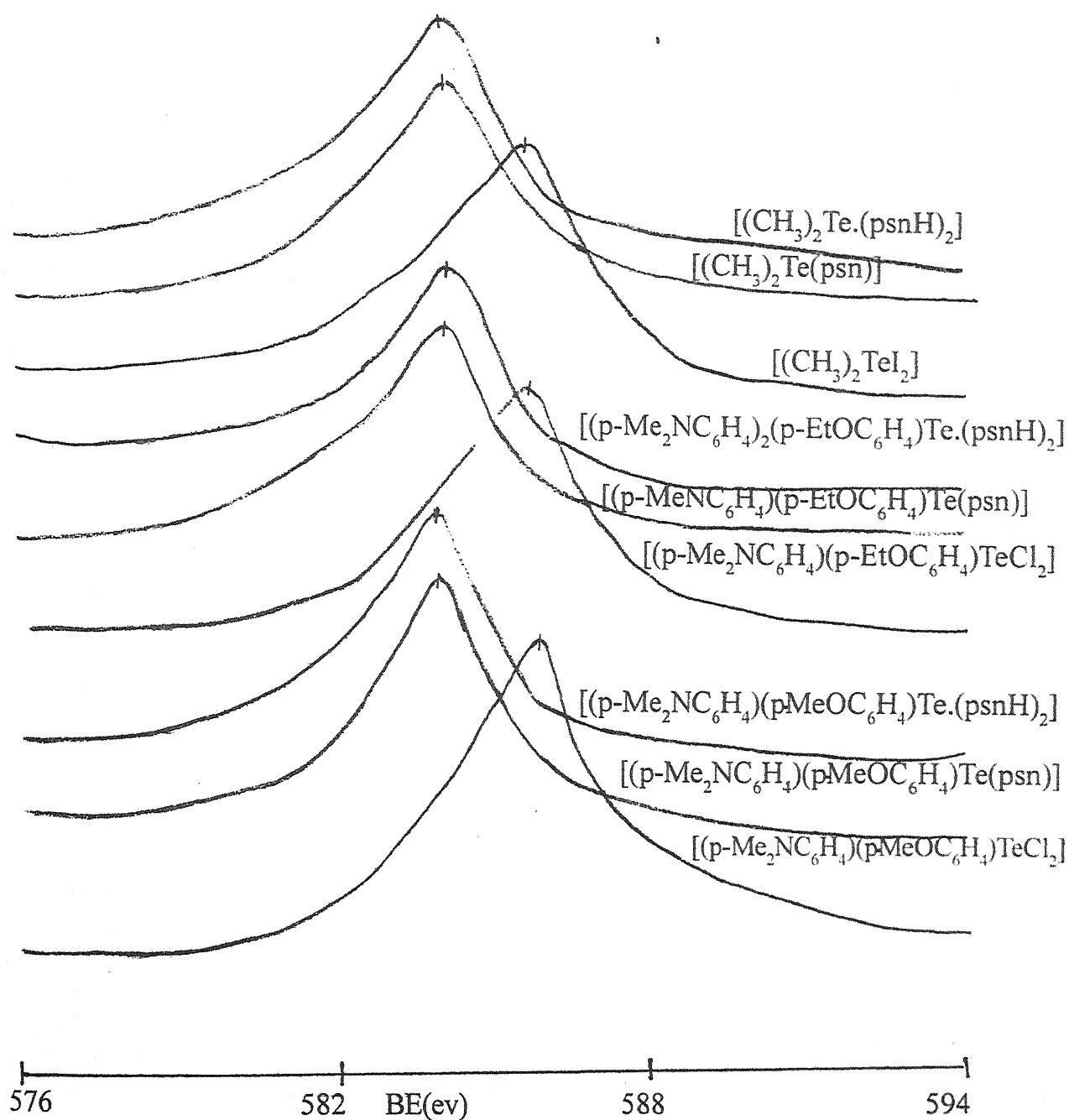


Fig 2 : Te 3d_{3/2} binding energies (ev) in R₂TeX₂; [R₂Te(psn)₂]
and [R₂Te.(psnH)₂] complexes

N1s photoelectron peak

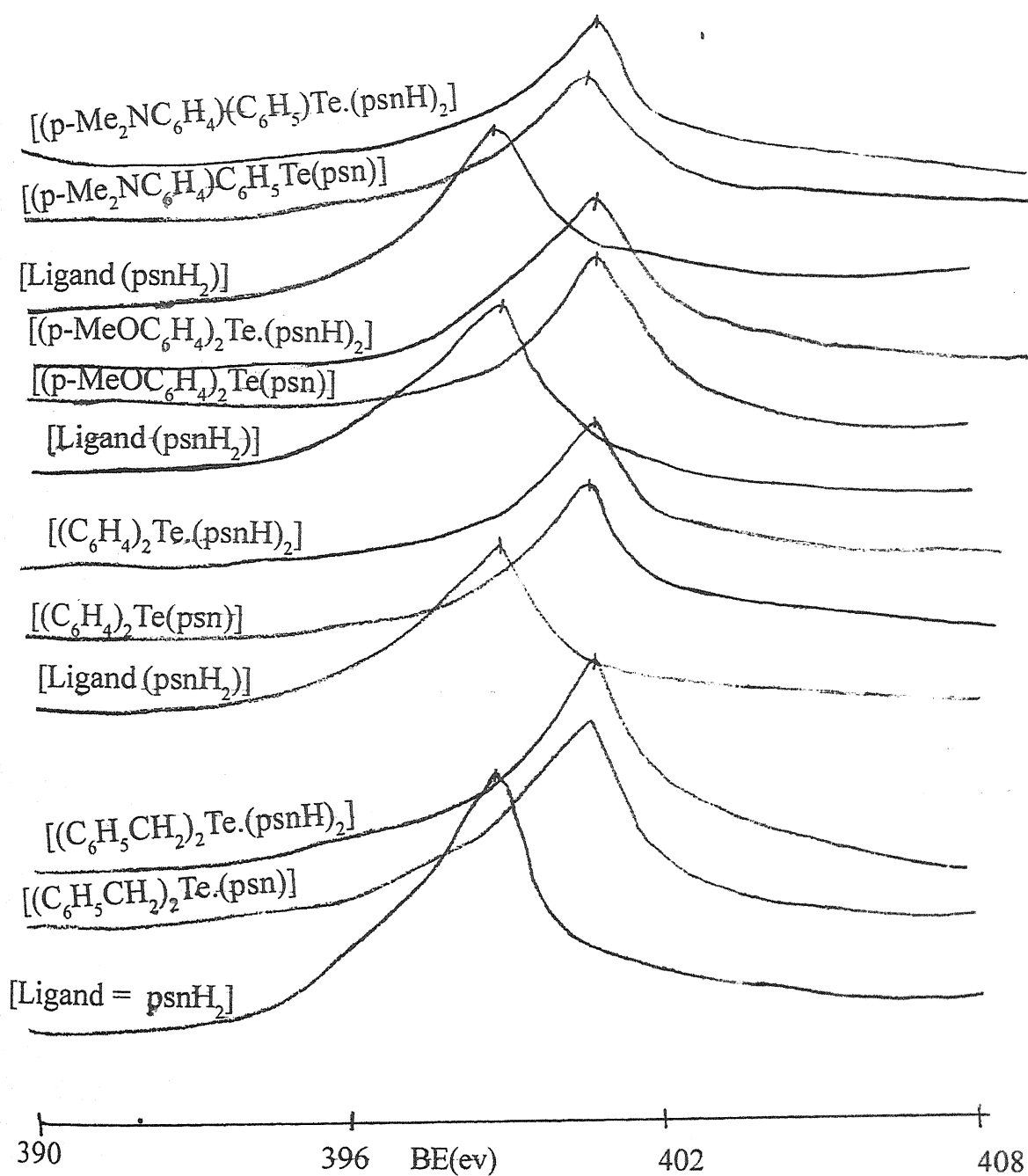


Fig 3 : N1s binding energies (ev) in Ligand, (psnH₂), [R₂Te(psn)] and [R₂Te.(psnH)₂] complexes

N1s photoelectron peak

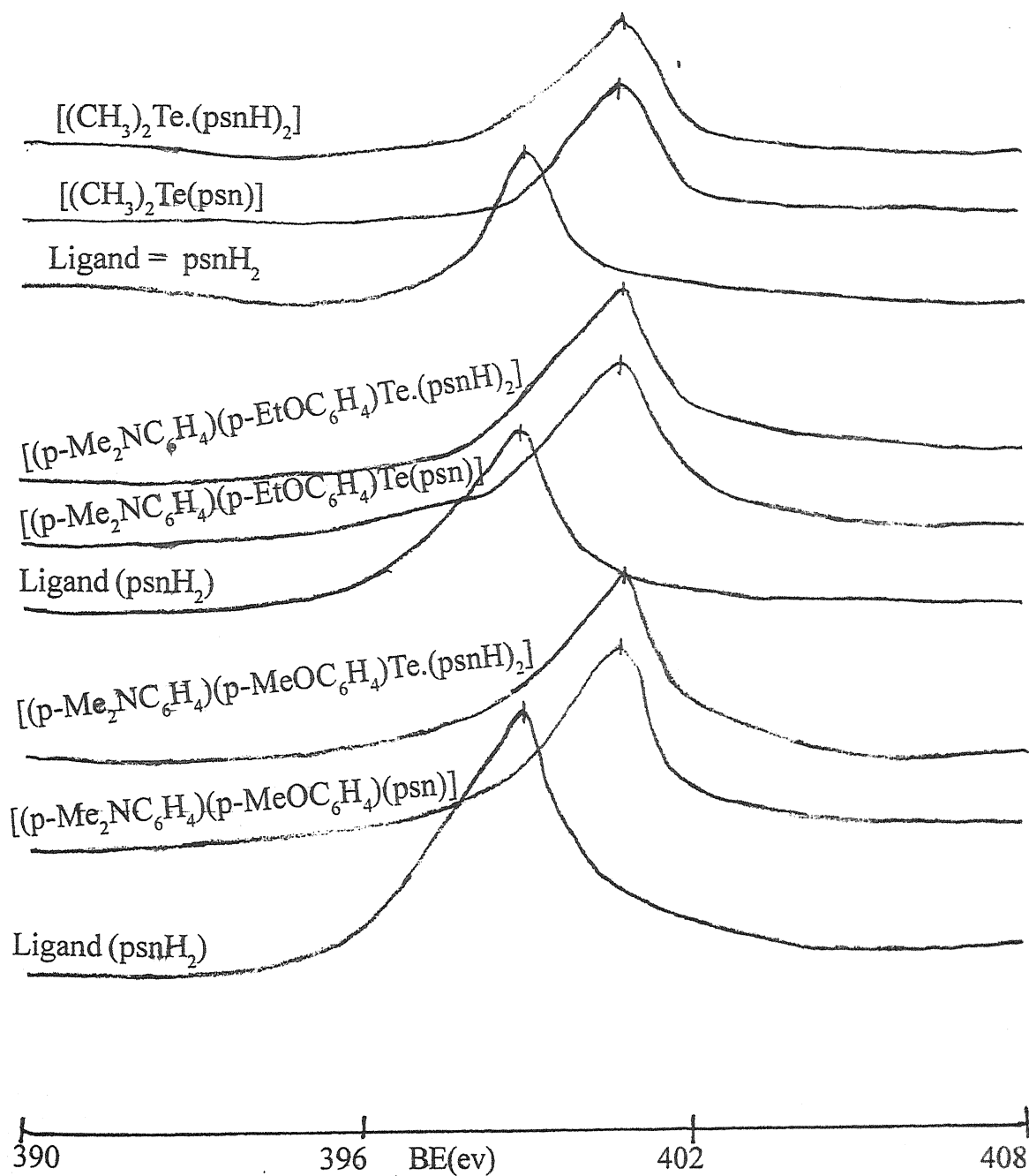


Fig 4 : N1s binding energies (ev) in Ligand, ($psnH_2$), $[R_2Te(psn)]$ and $[R_2Te.(psnH)_2]$ complexes

O1s photoelectron peak

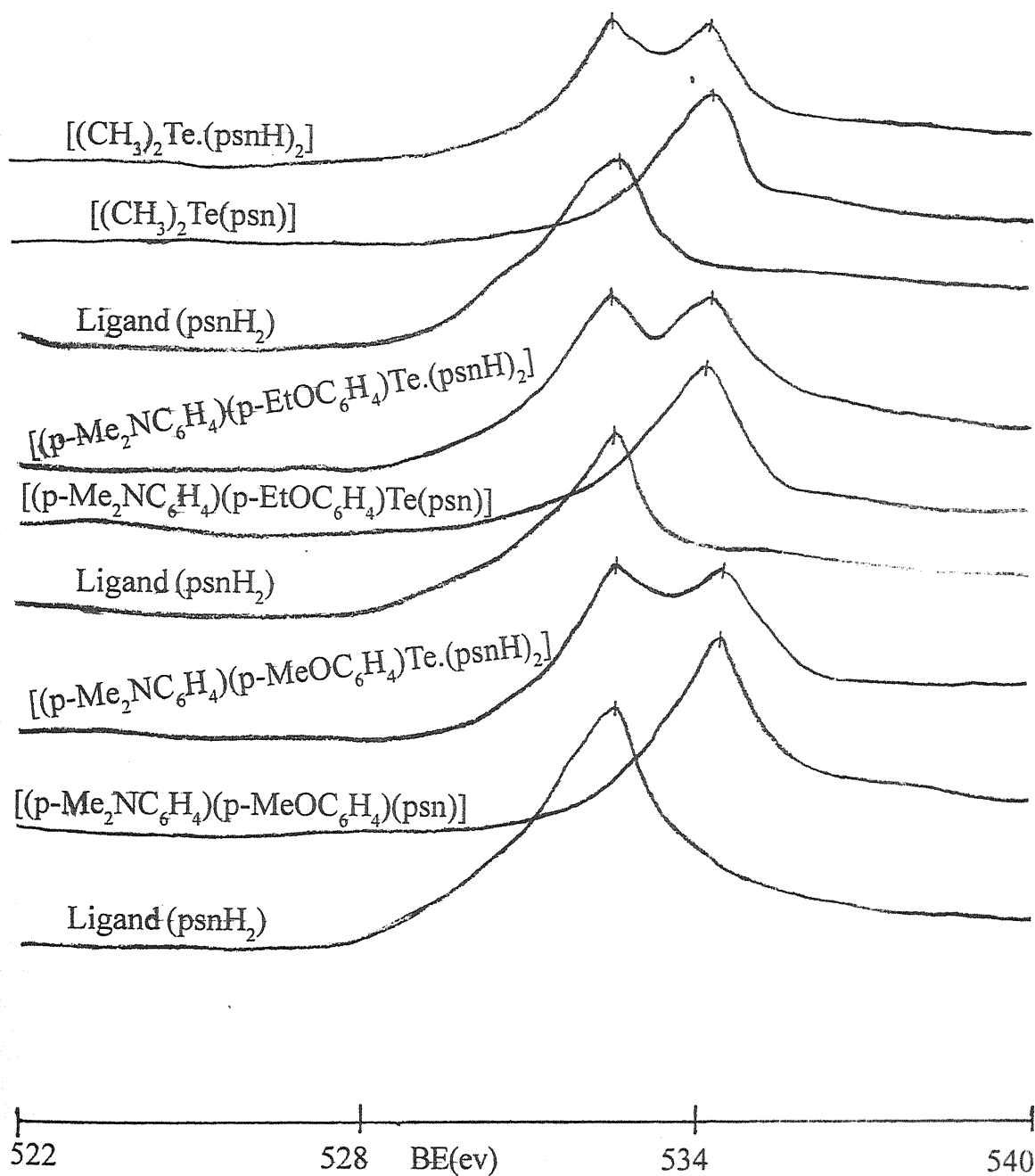


Fig 5 : O1s binding energies (ev) in Ligand, $[R_2Te(psn)]$ and $[R_2Te.(psnH)_2]$ complexes

O1s photoelectron peak

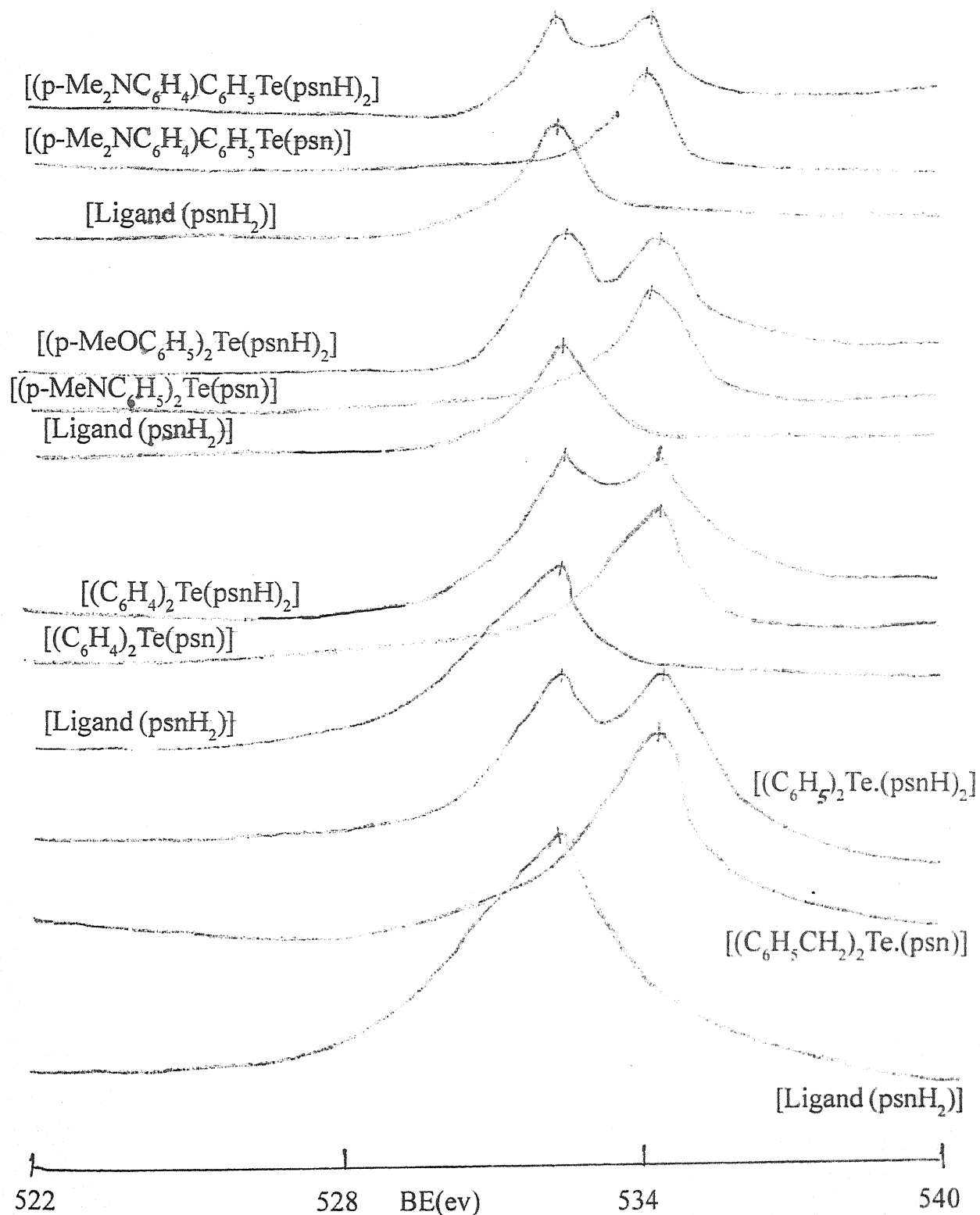


Fig 6 : O1s binding energies (ev) in Ligand, $[\text{R}_2\text{Te}(\text{psn})]$ and $[\text{R}_2\text{Te}(\text{psnH})_2]$ complexes

References :

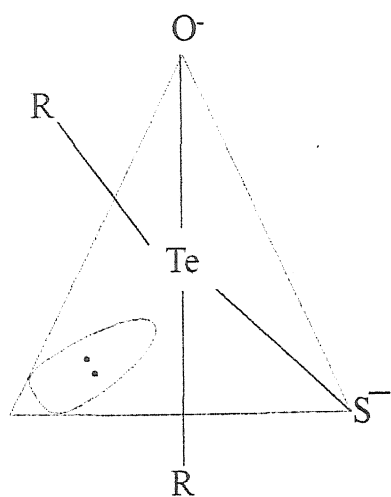
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CHAPTER - VI

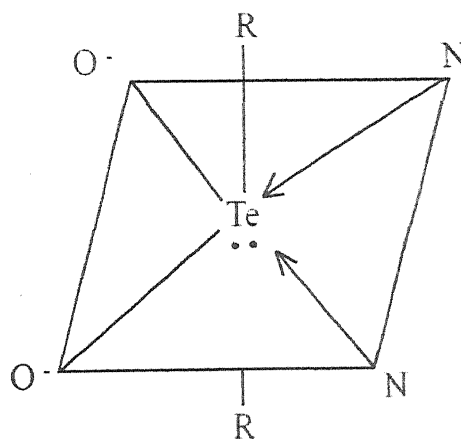
SUMMARY

The elements of group VI A have a general electronic configuration $[x] npx^2 npz^1$ (where x = inert gas core and $n = 2$ to 6 from oxygen to polonium) and tend to attain an inert gas configuration by gaining or sharing two electrons. Only few compounds are known which are more than 50% ionic for Te electropositive elements. The known formal oxidation state for tellurium are II and IV.

In chapter III, tellurium is in IV oxidation state in R_2TeX_2 which form with SamtrH₂ or 5Me – SamtrH₂ or 5Ph-SamtrH₂ ligand $[R_2Te(Satrm)]$ complexes and $[R_2Te.(SatrmH)_2]$ complexes and their established geometry are as given below:

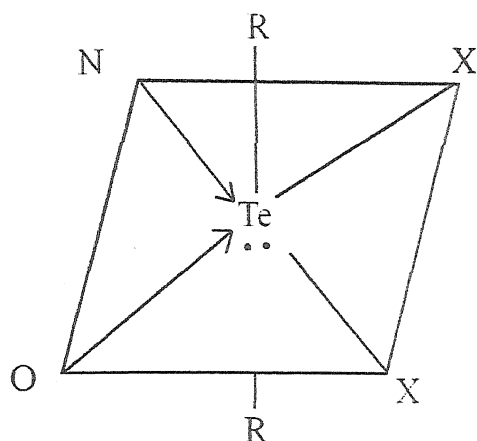


$[R_2Te(samtr)]$

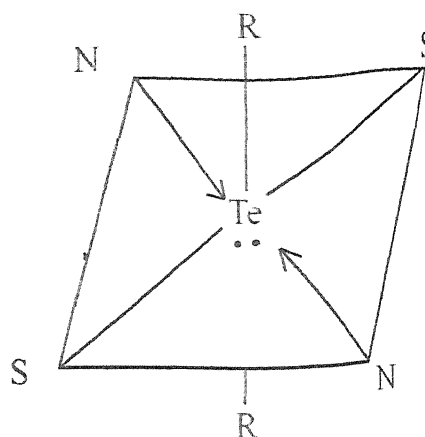


$[R_2Te (SamtrH)_2]$
(pseudooctahedral)

In chapter IV, the acceptor property of R_2TeX_2 with 3 – mercapto – 4 β – isatinylimino – 1, 2, 4 triazole in 1:1 and 1:2 molar ratio have been studied. it was established $[R_2Te(Istmtr)_2]$ and $[R_2TeX_2(IstmtrH)]$ molecular adducts with all octahedral i.e. (sp^3d^3) geometry as given below.

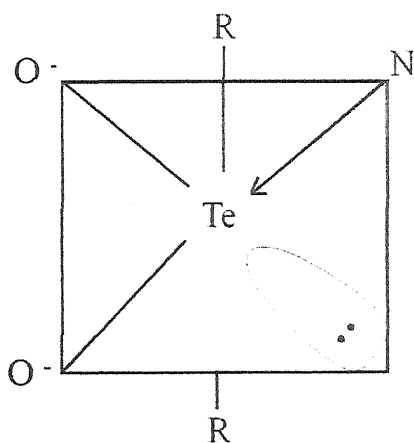


Geometry of $[R_2Te(IsamtrH)_2]$

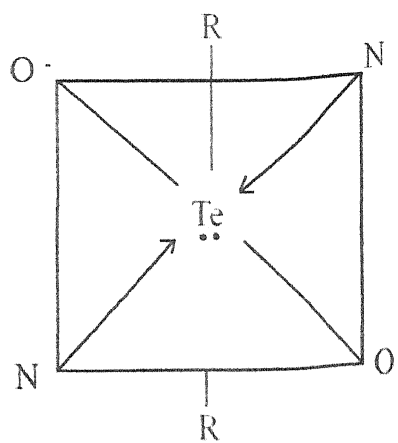


Geometry of $[R_2Te(Istmr)_2]$ complexes

In chapter V, the acceptor property of R_2TeX_2 with α - phenyl salicylaldimino methyl - β - naphthol in 1:1 and 1:2 molar ratio have been studied and it was established $[R_2Te(psn)]$ and $[R_2Te(psnH)_2]$ molecular adducts with all octahedral and pseudooctahedral geometry respectively.



Geometry of $[R_2Te(psn)]$
(octahedral)



Geometry of $[R_2Te(psnH)_2]$
(pseudooctahedral)

These prepared molecular adducts of R_2TeX_2 may be useful as antibacterial action¹, as medicine², as polymer³⁻⁴, as Therapeutic agents⁴⁻⁵, as oxi-

dants⁶⁻⁷, antiknocking agents⁶⁻⁷, in photochemical preparation⁶⁻⁷, photoconductors insecticides⁶⁻⁷, lubricating oil additives⁶⁻⁷, pharmacological agents⁶⁻⁷, corrosion inhibitors⁶⁻⁷ etc.

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